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# QUALITATIVE

# CHEMICAL ANALYSIS

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# CHEMICAL ANALYSIS

BY

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# PREFACE.

In the preparation of the last edition (1869) I undertook to rewrite this book in the hope of adapting it more thoroughly to the wants of our English students. To this I was led by a considerable experience in laboratory teaching, and also by the unanimous and authoritative advice of many friends. But I confess that I then took too broad a view of my duty, and in obedience to the author's wish I now abandon my reforms and adhere to the original text.

As usual, the author continues to keep his work abreast with the progress of science. Since the publication of the last translation (Sixth English Edition, 1864) he has revised all parts of the work, the pages on Rare Metals and Alkaloids showing the greatest alterations. Several new figures will be noticed, and the old spectrum table has been replaced by a fresh one.

A. V.

SCHOOL OF CHEMISTRY,
20, GREAT MARLBOROUGH STREET,
*June*, 1872.

# CONTENTS.

## PART I.

## INTRODUCTORY PART.

### PRELIMINARY REMARKS.


PAGE

Definition, general principles, objects, utility, and importance of qualitative chemical analysis. Conditions and requirements for a successful study of that science . . . . . 1


### SECTION I.


Operations, § 1 . . . . . 3
1. Solution, § 2 . . . . . 3
2. Crystallization, § 3 . . . . . 5
3. Precipitation, § 4 . . . . . 6
4. Filtration, § 5 . . . . . 7
5. Decantation, § 6 . . . . . 8
6. Washing, § 7 . . . . . 9
7. Dialysis, § 8 . . . . . 9
8. Evaporation, § 9 . . . . . 11
9. Distillation, § 10 . . . . . 12
10. Ignition, § 11 . . . . . 13
11. Sublimation, § 12 . . . . . 13
12. Fusion, § 13 . . . . . 14
13. Deflagration, § 14 . . . . . 15
14. The use of the blowpipe, § 15 . . . . . 15
15. The use of lamps, particularly of gas lamps, § 16 . . . . . 19
16. Observation of the coloration of flame by certain bodies, and spectrum analysis, § 17 . . . . . 26


*Appendix to the First Section.*


Apparatus, § 18 . . . . . 31


### SECTION II.


Reagents, § 19 . . . . . 32


#### A. Reagents in the wet way.


I. Simple solvents.
1. Water, § 20 . . . . . 35
2. Alcohol, § 21 . . . . . 35
3. Ether, § 22 . . . . . 36
4. Chloroform . . . . . 36
5. Sulphide of carbon . . . . . 36

PAGE

II. ACIDS AND HALOGENS, § 23.

*a. Oxygen acids.*

1. Sulphuric acid, § 24 . . . . . 37
2. Nitric acid, § 25 . . . . . 39
3. Acetic acid, § 26 . . . . . 39
4. Tartaric acid, § 27 . . . . . 40

*b. Hydrogen acids and halogens.*

1. Hydrochloric acid, § 28 . . . . . 40
2. Chlorine and chlorine water, § 29 . . . . . 42
3. Nitrohydrochloric acid, § 30 . . . . . 42
4. Hydrofluosilicic acid, § 31 . . . . . 43

*c. Sulphur acids.*

1. Hydrosulphuric acid, § 32 . . . . . 44

III. BASES AND METALS, § 33 . . . . . 48

*a. Oxygen bases.*

*a. Alkalies.*

1. Potassa and soda, § 34 . . . . . 49
2. Ammonia, § 35 . . . . . 50

*β. Alkaline earths.*

1. Baryta, § 36 . . . . . 51
2. Lime, § 37 . . . . . 52

*γ. Heavy metals and their oxides.*

1. Zinc, § 38 . . . . . 53
2. Iron . . . . . 53
3. Copper . . . . . 53
4. Hydrate of teroxide of bismuth, § 39 . . . . . 53

*b. Sulphur bases.*

1. Sulphide of ammonium, § 40 . . . . . 54
2. Sulphide of sodium, § 41 . . . . . 55

IV. SALTS.

*a. Salts of the alkalies.*

1. Sulphate of potassa, § 42 . . . . . 56
2. Phosphate of soda, § 43 . . . . . 56
3. Oxalate of ammonia, § 44 . . . . . 56
4. Acetate of soda, § 45 . . . . . 57
5. Carbonate of soda, § 46 . . . . . 57
6. Carbonate of ammonia, § 47 . . . . . 58
7. Bisulphite of soda, § 48 . . . . . 59
8. Nitrite of potassa, § 49 . . . . . 59
9. Bichromate of potassa, § 50 . . . . . 60
10. Antimonate of potassa, § 51 . . . . . 60
11. Molybdate of ammonia, § 52 . . . . . 60
12. Chloride of ammonium, § 53 . . . . . 61
13. Cyanide of potassium, § 54 . . . . . 62
14. Ferrocyanide of potassium, § 55 . . . . . 63
15. Ferricyanide of potassium, § 56 . . . . . 63
16. Sulphocyanide of potassium, § 57 . . . . . 63

*b. Salts of the alkaline earths.*

1. Chloride of barium, § 58 . . . . . 64
2. Nitrate of baryta, § 59 . . . . . 65
3. Carbonate of baryta, § 60 . . . . . 65
4. Sulphate of lime, § 61 . . . . . 65
5. Chloride of calcium, § 62 . . . . . 66
6. Sulphate of magnesia, § 63 . . . . . 66

PAGE

*c. Salts of the oxides of the heavy metals.*

1. Sulphate of iron, § 64 . . . . . 67
2. Sesquichloride of iron, § 65 . . . . . 67
3. Nitrate of silver, § 66 . . . . . 68
4. Acetate of lead, § 67 . . . . . 68
5. Nitrate of suboxide of mercury, § 68 . . . . . 69
6. Chloride of mercury, § 69 . . . . . 69
7. Sulphate of copper, § 70 . . . . . 69
8. Protochloride of tin, § 71 . . . . . 70
9. Bichloride of platinum, § 72 . . . . . 70
10. Sodio-protochloride of palladium, § 73 . . . . . 71
11. Terchloride of gold, § 74 . . . . . 71

V. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

1. Test papers, § 75 . . . . . 71
2. Indigo solution . . . . . 73

B. REAGENTS IN THE DRY WAY.

I. *Fluxes and decomposing agents.*

1. Mixture of carbonate of soda and carbonate of potassa, § 76 . . 73
2. Hydrate of baryta, § 77 . . . . . 75
3. Fluoride of calcium, § 78 . . . . . 75
4. Nitrate of soda, § 79 . . . . . 75
5. Acid sulphate of potassa, § 80 . . . . . 76

II. *Blowpipe reagents.*

1. Carbonate of soda, § 81 . . . . . 76
2. Cyanide of potassium, § 82 . . . . . 77
3. Biborate of soda, § 83 . . . . . 77
4. Phosphate of soda and ammonia, § 84 . . . . . 78
5. Nitrate of cobalt, § 85 . . . . . 79

SECTION III.

REACTIONS, § 86 . . . . . 80

A. REACTIONS OF THE METALLIC OXIDES AND THEIR RADICALS, § 87 . 80

FIRST GROUP, § 88 . . . . . 81

*a.* Potassa, § 89 . . . . . 82
*b.* Soda, § 90 . . . . . 83
*c.* Ammonia, § 91 . . . . . 85
Recapitulation and remarks, § 92 . . . . . 86
Oxide of cæsium, oxide of rubidium, lithia, § 93 . . . . . 87

SECOND GROUP, § 94 . . . . . 89

*a.* Baryta, § 95 . . . . . 89
*b.* Strontia, § 96 . . . . . 91
*c.* Lime, § 97 . . . . . 93
*d.* Magnesia, § 98 . . . . . 94
Recapitulation and remarks, § 99 . . . . . 96

THIRD GROUP, § 100 . . . . . 98

*a.* Alumina, § 101 . . . . . 99
*b.* Sesquioxide of chromium, § 102 . . . . . 101
Recapitulation and remarks, § 103 . . . . . 102
Beryllia, thoria, zirconia, yttria, oxide of erbium, oxides of cerium, oxide of lanthanium, oxide of didymium, titanic acid, tantalic acid, niobic acid, § 104 . . . . . 103

PAGE

FOURTH GROUP, § 105 . . . . . 111

*a.* Oxide of zinc, § 106 . . . . . 111
*b.* Protoxide of manganese, § 107 . . . . . 113
*c.* Protoxide of nickel, § 108 . . . . . 115
*d.* Protoxide of cobalt, § 109 . . . . . 117
*e.* Protoxide of iron, § 110 . . . . . 119
*f.* Sesquioxide of iron, § 111 . . . . . 120
Recapitulation and remarks, § 112 . . . . . 122
Oxides of uranium, thallium, indium, and vanadium, § 113 . . . 124

FIFTH GROUP. § 114 . . . . . 127

*First Division.*

*a.* Oxide of silver, § 115 . . . . . 127
*b.* Suboxide of mercury, § 116 . . . . . 128
*c.* Oxide of lead, § 117 . . . . . 130
Recapitulation and remarks, § 118 . . . . . 131

*Second Division.*

*a.* Oxide of mercury, § 119 . . . . . 132
*b.* Oxide of copper, § 120 . . . . . 133
*c.* Teroxide of bismuth, § 121 . . . . . 136
*d.* Oxide of cadmium, § 122 . . . . . 137
Recapitulation and remarks, § 123 . . . . . 138
Protoxide of palladium, sesquioxide of rhodium, oxides of osmium and ruthenium, § 124 . . . . . 139

SIXTH GROUP, § 125 . . . . . 142

*First Division.*

*a.* Teroxide of gold, § 126 . . . . . 143
*b.* Binoxide of platinum, § 127 . . . . . 144
Recapitulation and remarks, § 128 . . . . . 145

*Second Division.*

*a.* Protoxide of tin, § 129 . . . . . 145
*b.* Binoxide of tin, § 130 . . . . . 147
*c.* Teroxide of antimony, § 131 . . . . . 148
*d.* Arsenious acid, § 132 . . . . . 152
*e.* Arsenic acid, § 133 . . . . . 161
Recapitulation and remarks, § 134 . . . . . 162
Oxide of iridium, oxides of molybdenum, tungsten, tellurium, and selenium, § 135 . . . . . 166

B. REACTIONS OF THE ACIDS AND THEIR RADICALS, § 136 . . . 169

Classification of acids in groups . . . . . 170

I. INORGANIC ACIDS.

FIRST GROUP, § 137 . . . . . 170

*First Division.*

Chromic acid, § 138 . . . . . 171
Sulphurous, hyposulphurous, iodic acid, § 139 . . . . . 173

*Second Division.*

Sulphuric acid, § 140 . . . . . 174
Hydrofluosilicic acid, § 141 . . . . . 176

*Third Division.*

PAGE
*a.* Phosphoric acid, § 142 . . . . . 176
Bibasic and monobasic phosphoric acid, § 143 . . . . 180
*b.* Boracic acid, § 144 . . . . . 180
*c.* Oxalic acid, § 145 . . . . . 182
*d.* Hydrofluoric acid, § 146 . . . . . 183
Recapitulation and remarks, § 147 . . . . . 186
Phosphorous acid, § 148 . . . . . 187

*Fourth Division.*

*a.* Carbonic acid, § 149 . . . . . 187
*b.* Silicic acid, § 150 . . . . . 189
Recapitulation and remarks, § 151 . . . . . 191

SECOND GROUP.

*a.* Hydrochloric acid, § 152 . . . . . 191
*b.* Hydrobromic acid, § 153 . . . . . 193
*c.* Hydriodic acid, § 154 . . . . . 195
*d.* Hydrocyanic acid, § 155 . . . . . 197
Hydroferrocyanic and hydroferricyanic acid . . . . 199
*e.* Hydrosulphuric acid, § 156 . . . . . 200
Recapitulation and remarks, § 157 . . . . . 202
Nitrous, hypochlorous, chlorous, hypophosphorous acid, § 158 . . 204

THIRD GROUP.

*a.* Nitric acid, § 159 . . . . . 206
*b.* Chloric acid, § 160 . . . . . 207
Recapitulation and remarks, § 161 . . . . . 208
Perchloric acid, § 162 . . . . . 209

II. ORGANIC ACIDS.

FIRST GROUP.

*a.* Oxalic acid . . . . . 209
*b.* Tartaric acid, § 163 . . . . . 209
*c.* Citric acid, § 164 . . . . . 211
*d.* Malic acid, § 165 . . . . . 212
Recapitulation and remarks, § 166 . . . . . 214
Racemic acid, § 167 . . . . . 215

SECOND GROUP.

*a.* Succinic acid, § 168 . . . . . 215
*b.* Benzoic acid, § 169 . . . . . 217
Recapitulation and remarks, § 170 . . . . . 217

THIRD GROUP.

*a.* Acetic acid, § 171 . . . . . 218
*b.* Formic acid, § 172 . . . . . 219
Recapitulation and remarks, § 173 . . . . . 220
Lactic, propionic, and butyric acids, § 174 . . . . . 221

# PART II.

## COURSE OF ANALYSIS.

PAGE

Preliminary remarks on the course of qualitative analysis in general, and on the plan of this part of the present work in particular . . . 223

## SECTION I.

### PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. Preliminary examination, § 175 . . . . . 225

A. The substance is solid.

1. It is neither a pure metal nor an alloy, § 176 . . . . 225
2. It is a metal or an alloy, § 177 . . . . . 231

B. The substance is a fluid, § 178 . . . . . 231

II. The solution of bodies, or classification of substances according to their deportment with certain solvents, § 179 . . . . . 232

A. The substance is neither a metal nor an alloy, § 180 . . . 233

B. The substance is a metal or an alloy, § 181 . . . . . 235

### III. Actual Examination.

#### SIMPLE COMPOUNDS.

A. *Substances soluble in water.*

Detection of the base, § 182 . . . . . 236

Detection of the acid.

I. Detection of inorganic acids, § 183 . . . . . 241

II. Detection of organic acids, § 184 . . . . . 243

B. *Substances insoluble or sparingly soluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid.*

Detection of the base, § 185 . . . . . 245

Detection of the acid.

I. Detection of inorganic acids, § 186 . . . . . 247

II. Detection of organic acids, § 187 . . . . . 249

C. *Substances insoluble or sparingly soluble in water, hydrochloric acid, nitric acid, or nitrohydrochloric acid.*

Detection of the base and the acid, § 188 . . . . . 249

#### COMPLEX COMPOUNDS.

A. *Substances soluble in water or in hydrochloric acid, nitric acid, or nitrohydrochloric acid.*

Detection of the bases, § 189.

I. Solution in water.

Detection of silver and suboxide of mercury . . . . . 251

II. Solution in hydrochloric acid or aqua regia . . . . . 254

III. Solution in nitric acid.

Detection of silver and suboxide of mercury . . . . . 254

Treatment with hydrosulphuric acid, precipitation of the metallic oxides of Group V., 2nd division, and of Group VI., § 190 . . . . 255

Treatment of the precipitate produced by hydrosulphuric acid with sulphide of ammonium; separation of the 2nd division of Group V. from Group VI., § 191 . . . . . 256

PAGE

Detection of the metals of Group VI. Arsenic, antimony, tin, gold, platinum, § 192 . . . . . 257
Detection of the metallic oxides of Group V., 2nd division. Oxide of lead, teroxide of bismuth, oxide of copper, oxide of cadmium, oxide of mercury, § 193 . . . . . 260
Precipitation with sulphide of ammonium, detection and separation of the oxides of Groups III. and IV. Alumina, sesquioxide of chromium, oxide of zinc, protoxide of manganese, protoxide of nickel, protoxide of cobalt, proto- and sesquioxide of iron, and also of those salts of the alkaline earths which are precipitated by ammonia from their solution in hydrochloric acid: phosphates, borates, oxalates, silicates, and fluorides, § 194 . . . . . 262
Separation and detection of the oxides of Group II., which are precipitated by carbonate of ammonia in presence of chloride of ammonium. Baryta, strontia, lime, § 195 . . . . . 269
Examination for magnesia, § 196 . . . . . 270
Examination for potassa and soda, § 197 . . . . . 271
Examination for ammonia, § 198 . . . . . 272
A. 1. Substances soluble in water.
Detection of acids.
I. In the absence of organic acids, § 199 . . . . . 272
II. In presence of organic acids, § 200 . . . . . 275
A. 2. Substances insoluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid.
Detection of acids.
I. In the absence of organic acids, § 201 . . . . . 277
II. In presence of organic acids, § 202 . . . . . 278
B. *Substances insoluble or sparingly soluble both in water and acids.*
Detection of the bases, acids, and non-metallic elements, § 203 . . 278

## SECTION II.

### PRACTICAL COURSE IN PARTICULAR CASES.

I. Special method of effecting the analysis of cyanides, ferrocyanides, &c., insoluble in water, § 204 . . . . . 282
II. Analysis of silicates, § 205 . . . . . 283
A. Silicates decomposable by acids, § 206 . . . . . 284
*a.* Decomposable by hydrochloric or nitric acid.
*b.* Decomposable by concentrated sulphuric acid.
B. Silicates which are not decomposed by acids, § 207 . . . . 286
C. Silicates which are partially decomposed by acids, § 208 . . . 288
III. Analysis of natural waters, § 209 . . . . . 288
A. Analysis of potable waters, § 210 . . . . . 289
B. Analysis of mineral waters, § 211 . . . . . 292
1. Examination of the water.
*a.* Operations at the spring, § 212 . . . . . 293
*b.* Operations in the laboratory, § 213 . . . . . 294
2. Examination of the sinter-deposit, § 214 . . . . . 298
IV. Analysis of soils, § 215 . . . . . 300
1. Preparation and examination of the aqueous extract, § 216 . . 301
2. Preparation and examination of the acid extract, § 217 . . . 302
3. Examination of the inorganic constituents insoluble in water and acids, § 218 . . . . . 303
4. Examination of the organic constituents of the soil, § 219 . . 303
V. Detection of inorganic substances in presence of organic substances, § 220 304
1. General rules for the detection of inorganic substances in presence of organic matters, § 221 . . . . . 304
2. Detection of inorganic poisons in articles of food, in dead bodies, &c., in chemico-legal cases, § 222 . . . . . 308

PAGE

I. Detection of arsenic, § 223 . . . . . 308
A. Detection of undissolved arsenious acid . . . . . 308
B. Detection of soluble arsenical and other metallic compounds, by means of dialysis, § 224 . . . . . 309
C. Method for the detection of arsenic in whatever form of combination it may exist, which allows also a quantitative determination of that poison, and permits at the same time the detection of other metallic poisons which may be present, § 225 . . . . . 310
II. Detection of hydrocyanic acid, § 226 . . . . . 316
III. Detection of phosphorus, § 227 . . . . . 318
3. Examination of the inorganic constituents of plants, animals, or parts of the same, of manures, &c. (analysis of ashes), § 228 . . . 323
A. Preparation of the ash . . . . . 323
B. Examination of the ash . . . . . 324
*a.* Examination of the part soluble in water . . . . . 324
*b.* Examination of the part soluble in hydrochloric acid . . . 325
*c.* Examination of the residue insoluble in hydrochloric acid . . 326

## SECTION III.

### EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. Additional remarks to the preliminary examination, To §§ 175—178 . 327
II. Additional remarks to the solution of substances, &c., To §§ 179—181 327
III. Additional remarks to the actual examination, To §§ 182—204.
A. General review and explanation of the analytical course.
*a.* Detection of the bases . . . . . 329
*b.* Detection of the acids . . . . . 332
B. Special remarks and additions to the systematic course of analysis.
To § 189 . . . . . 335
§§ 190 and 191 . . . . . 337
§ 192 . . . . . 338
§ 193 . . . . . 338
§ 194 . . . . . 339
§§ 195—198 . . . . . 340
§ 203 . . . . . 340
§ 204 . . . . . 341

## APPENDIX.

I. Deportment of the most important medicinal alkaloids with reagents, and systematic method of effecting the detection of these substances, § 229 . . . . . 343
A. General reagents for alkaloids, § 230 . . . . . 343
B. Reactions of individual alkaloids . . . . . 343
I. Volatile alkaloids.
1. Nicotina, § 231 . . . . . 346
2. Conia, § 232 . . . . . 347
II. Non-volatile alkaloids.

#### FIRST GROUP.

Morphia, § 233 . . . . . 348

#### SECOND GROUP.

*a.* Narcotina, § 234 . . . . . 351
*b.* Quina, § 235 . . . . . 353
*c.* Cinchonia, § 236 . . . . . 354
Recapitulation and remarks, § 237 . . . . . 355

THIRD GROUP.

PAGE

*a.* Strychnia, § 238 . . . . . 356
*b.* Brucia, § 239 . . . . . 358
*c.* Veratria, § 240 . . . . . 359
*d.* Atropia, § 241 . . . . . 360
Recapitulation and remarks, § 242 . . . . . 361
C. Reactions of non-azotized bodies, allied to alkaloids.
*a.* Salicine, § 243 . . . . . 362
*b.* Digitaline, § 244 . . . . . 362
*c.* Picrotoxine, § 245 . . . . . 363
Systematic course for the detection of alkaloids, and of salicine, digitaline, and picrotoxine.
I. Detection of the non-volatile alkaloids, &c., in solutions supposed to contain only one of these substances, § 246 . . . . . 364
II. Detection of the non-volatile alkaloids, &c., in solutions supposed to contain several or all of these substances, § 247 . . . . . 366
III. Detection of alkaloids and of digitaline and picrotoxine in presence of coloring and extractive vegetable or animal matters . . . . . 368
1. STAS's method of detecting poisonous alkaloids (also digitaline and picrotoxine), modified by OTTO, § 248 . . . . . 369
2. Methods of detecting strychnia, based upon the use of chloroform, § 249 . . . . . 372
3. Method of detecting strychnia in beer, by GRAHAM and HOFMANN, § 250 . . . . . 373
4. Separation by dialysis, § 251 . . . . . 373
II. General plan of the order in which substances should be analyzed for practice, § 252 . . . . . 373
III. Arrangement of the results of analyses performed for practice, § 253 . 375
IV. Table of the solubility of compounds, § 254 . . . . . 378

INDEX . . . . . 383

# PART I.

# INTRODUCTORY.

## PRELIMINARY REMARKS.

### DEFINITION, GENERAL PRINCIPLES, OBJECTS, UTILITY, AND IMPORTANCE OF QUALITATIVE CHEMICAL ANALYSIS—CONDITIONS AND REQUIREMENTS FOR A SUCCESSFUL STUDY OF THAT SCIENCE.

CHEMISTRY is the science which treats of the various materials entering into the structure of the earth, their composition and decomposition, their mutual relations and their deportment in general. A special branch of this science is designated *Analytical Chemistry*, inasmuch as it pursues a distinct and definite object—viz. the analysis of compound bodies, and the determination of their component elements. Analytical chemistry, again, is subdivided into two branches—viz. *qualitative analysis*, which simply studies the nature and properties of the component parts of bodies; and *quantitative analysis*, which ascertains the quantity of every individual constituent present. The office of qualitative analysis, therefore, is to exhibit the constituent parts of a substance of unknown composition in forms of known composition, from which the constitution of the body examined and the presence of its several component elements may be positively inferred. The efficiency of its method depends upon two conditions—viz., 1st, it must attain the object in view with unerring certainty, and 2nd, it must attain it in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation in forms which will permit the most accurate estimate of their weight, or to effect by other means the determination of their quantity.

These different ends are, of course, attained respectively by very different ways and means. The study of qualitative analysis must, therefore, be pursued separately from that of quantitative analysis, and must naturally precede it.

Having thus generally defined the meaning and scope of qualitative analysis, we have now still to consider, in the first place, the preliminary information required to qualify students for a successful cultivation of this branch of science, the rank which it holds in the domain of chemistry, the bodies that fall within the sphere of its operations, and its utility and importance: and, in the second place, the principal parts into which its study is divided.

It is, above all, *absolutely indispensable* for a successful pursuit of

qualitative investigations that the student should possess some knowledge of the chemical elements, and of their most important combinations, as well as of the principles of chemistry in general; and that he should combine with this knowledge some readiness in the apprehension of chemical processes. The practical part of this science demands moreover strict order, great cleanness and neatness, and a certain skill in manipulation. If the student joins to these qualifications the habit of invariably ascribing the failures with which he may happen to meet to some error or defect in his operations, or, in other words, to the absence of some condition or other indispensable to the success of the experiment —and a firm reliance on the immutability of the laws of nature cannot fail to create this habit—he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we have to look upon it also as one of the main pillars upon which the entire structure of the science rests, since it is of almost equal importance for all branches of theoretical as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the pharmaceutist, the mineralogist, the rational farmer, the manufacturer, and many others derive from it.

This consideration would surely in itself be sufficient reason to recommend a thorough and diligent study of this branch of science, even if its cultivation lacked those attractions which yet it unquestionably possesses for every one who devotes himself zealously and ardently to it. The human mind is constantly striving for the attainment of truth; it delights in the solution of problems; and where do we meet with a greater variety of them, more or less difficult of solution, than in the province of chemistry? But as a problem to which, after long pondering, we fail to discover the key, wearies and discourages the mind; so, in like manner, do chemical investigations, if the object in view is not attained—if the results do not bear the stamp of truth, of unerring certainty. A half-knowledge is therefore, as indeed in every department of science, but more especially here, to be considered worse than no knowledge at all; and a mere superficial cultivation of chemical analysis is consequently to be particularly guarded against.

A qualitative investigation may be made with a twofold view—viz., either, 1st, to prove that a certain body is or is not contained in a substance, *e.g.*, lime in spring-water; or, 2nd, to ascertain all the constituents of a chemical compound or mixture. Any substance may of course become the object of a chemical analysis.

But all elements are not equally important for the purposes of practical chemistry, a certain number of them only being found more widely disseminated in nature, and being more generally employed in pharmacy, in the arts and manufactures, and in agriculture, whilst the others are met with only as constituents of rarely occurring minerals; the elements of the former class alone, therefore, and the more important of their compounds, will be considered more fully in the present work, whilst those of the latter class will be discussed more briefly and in a manner to enable the learner to separate, without difficulty, the study of the former from that of the latter. This arrangement will serve to render the study of the science more easy to beginners, and to lighten the labors of practical chemists.

The study of qualitative analysis is most properly divided into four principal parts—viz.,

1. CHEMICAL OPERATIONS.
2. REAGENTS AND THEIR USES.
3. REACTIONS, OR DEPORTMENT OF THE VARIOUS BODIES WITH REAGENTS.
4. SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.

It will now be readily understood that the pursuit of chemical analysis requires practical skill and ability as well as theoretical knowledge; and that, consequently, a mere speculative study of that science can be as little expected to lead to success as purely empirical experiments. To attain the desired end, theory and practice must be combined.

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# SECTION I.

## OPERATIONS.

### § 1.

THE operations of analytical chemistry are essentially the same as those of synthetical chemistry, though modified to a certain extent to adapt them to the different object in view, and to the small quantities operated upon in analytical investigations.

The following are the principal operations in qualitative analysis.

### § 2.

### 1. SOLUTION.

The term *solution*, in its widest sense, denotes the perfect union of a body, no matter whether gaseous, liquid, or solid, with a fluid, resulting in a homogeneous liquid. However, where the substance dissolved is gaseous, the term *absorption* is more properly made use of; and the solution of one fluid in another is more generally called a *mixture*. The application of the term solution, in its usual and more restricted sense, is confined to the perfect union of a solid body with a fluid.

A solution is the more readily effected the more minutely the body to be dissolved is divided. The fluid by means of which the solution is effected, is called the *solvent*. We call the solution *chemical*, where the solvent enters into chemical combination with the substance dissolved; *simple*, where no definite combination takes place.

In a *simple* solution the dissolved body exists in the free state, and retains all its original properties, except those dependent on its form and cohesion; it separates unaltered when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the fluid. On evaporating the water, the salt is left behind in its original form. A simple solution is called *saturated* if the solvent has received as much as it can retain of the dissolved substance. But as fluids dissolve generally larger quantities of a substance the higher their temperature, the term saturated, as applied to *simple solutions*, is only relative, and refers invariably

to a certain temperature. It may be laid down as a general rule that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, which latter also has lost its original properties; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be accelerated by elevation of temperature; and this is indeed usually the case, since heat generally promotes the action of bodies upon each other. But the quantity of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference of temperature—the combining proportions of substances being invariable and altogether independent of the gradations of temperature.

The reason of this is, that in a chemical solution the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case also said to be saturated or, more properly, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization.

The substances which produce chemical solutions are, in most cases, either acids or alkalies. With few exceptions, they have first to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present; *e.g.*, if solution of acetic acid in water is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and then a simple solution of the new-formed acetate of lead in the water of the menstruum.

In pharmacy solutions are often made in a porcelain mortar, by triturating the body to be dissolved with the solvent added gradually in small quantities at a time; in chemical laboratories solutions are rarely made in this manner, but generally by digesting or heating the substance to be dissolved with the fluid in beakers, flasks, test-tubes, or dishes. In the preparation of chemical solutions the best way generally is to mix the body to be dissolved in the first place with water (or with whatever other indifferent fluid may happen to be used), and then gradually add the chemical agent. By this course of proceeding a large excess of the latter is avoided, an over-energetic action guarded against, the process greatly facilitated, and complete solution ensured, which is a matter of some importance, as it will not seldom happen in chemical combinations that the product formed refuses to dissolve if an excess of the chemical solvent is present; in which case the molecules first formed of the new salt, being insoluble in the menstruum present, gather round and enclose the particles still unacted on, weakening thereby or preventing altogether further chemical action upon them. Thus, for instance, witherite (carbonate of baryta) dissolves readily if water is poured upon the pulverised mineral and hydrochloric acid gradually added; but it dissolves with difficulty and imperfectly if it is projected into a concentrated solution of hydrochloric acid in water; since chloride of barium will indeed dissolve in water, but not in hydrochloric acid.

CRYSTALLIZATION and PRECIPITATION are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both generally depend on the same cause, viz., on the want of a solvent, it is impossible to assign exact limits to either; in many cases they merge into one another. We must, however, consider them separately here, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

## § 3.

### 2. CRYSTALLIZATION.

We understand by the term *crystallization*, in a more general sense, every operation or process whereby bodies are made to pass from the fluid to the solid state, and to assume certain fixed, mathematically definable, regular forms. But as these forms, which we call *crystals*, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term crystallization the accessory idea of a slow separation—of a gradual conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate particles of bodies; it can only take place, therefore, if these particles possess perfect freedom of motion, and thus in general only when a substance passes from the fluid or gaseous to the solid state. Those instances in which the mere ignition, or the softening or moistening of a solid body, suffices to make the tendency of the particles to a regular arrangement (crystallization) prevail over the diminished force of cohesion—such as, for instance, the turning white and opaque of moistened barley-sugar—are to be regarded as exceptional cases.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat*, as in the case of fused metals; or *solvents*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of nitrate of potassa in water. In the first case we accordingly obtain crystals by cooling; in the second by evaporating; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of crystals are called *mother-liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We have recourse to crystallization mostly either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum. In many cases also the form of the crystals or their deportment in the air, viz., whether they remain unaltered or effloresce or deliquesce upon exposure to the air, will afford an excellent means of distinguishing between bodies otherwise resembling each other; for instance, between sulphate of soda and sulphate of potassa. The process of crystallization is usually effected in evaporating dishes or, for very small quantities, in watch-glasses.

In cases where the quantity of fluid to be operated upon is only small, the surest way of getting well-formed crystals is to let the fluid evaporate in the air or, better still, under a bell-glass, under which is

also placed an open vessel half-filled with concentrated sulphuric acid. Minute crystals are examined best with a lens or under the microscope.

§ 4.

### 3. Precipitation.

This operation differs from the preceding in this, that the dissolved body is converted to the solid state, not slowly and gradually, but suddenly, no matter whether the substance separating is crystalline or amorphous, whether it sinks to the bottom of the vessel or ascends or remains suspended in the liquid. Precipitation is either caused by a modification of the solvent—thus sulphate of lime separates immediately from its solution in water upon the addition of alcohol; or it ensues in consequence of the separation of an educt insoluble in the menstruum —thus metallic copper precipitates if a solution of chloride of copper is brought into contact with zinc, as this separates the copper from the chlorine, and the eliminated metal is insoluble in the water. Precipitation, lastly, takes place also where, by the action of simple or double chemical affinity, new compounds are formed which are insoluble in the menstruum; thus oxalate of lime precipitates upon addition of oxalic acid to a solution of acetate of lime; chromate of lead if chromate of potassa in solution is mixed with solution of nitrate of lead. In decompositions of this kind, induced by simple or double affinity, one of the new compounds remains generally in solution, and the same is sometimes the case also with the educt; thus in the instances just mentioned the chloride of zinc, the acetic acid, and the nitrate of potassa remain in solution. It may, however, happen also that both the product and the educt, or two products, precipitate, and that nothing remains in solution; this is the case, for instance, when a solution of sulphate of magnesia is mixed with baryta water, or when a solution of sulphate of silver is precipitated with chloride of barium.

Precipitation is resorted to for the same purposes as crystallization, viz., either to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we have recourse to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process is called the *precipitate*, and the substance which acts as the immediate cause of the separation is termed the *precipitant*. Various terms are applied to precipitates by way of particularising them according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, &c. Precipitates which appear pulverulent to the naked eye will often be seen when examined under the microscope to consist entirely of regular crystals; and such precipitates may frequently be distinguished from each other in this way.

The terms *turbid* and *turbidity*, or *cloudy* and *cloudiness*, are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally

be promoted by vigorously shaking the vessel; that of crystalline precipitates, by stirring the fluid and rubbing the inside of the vessel with a glass rod; lastly, elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is conducted, according to circumstances, either in test-tubes, flasks, beakers, or dishes.

The two operations described in §§ 5 and 6, viz. FILTRATION and DECANTATION, serve to effect the mechanical separation of fluids from matter suspended therein.

## § 5.

### 4. FILTRATION.

This operation consists simply in passing the fluid from which we wish to remove the solid particles mechanically suspended therein through a filtering apparatus, formed usually by a properly folded piece of unsized paper placed in a funnel. An apparatus of this description allows the fluid to trickle through with ease, whilst it completely retains the solid particles. We employ smooth filters and plaited filters; the former in cases where the separated solid substance is to be made use of, the latter in cases where it is simply intended to clear the solution. Smooth filters are prepared by double-folding a circular piece of paper, with the folds at right angles; they must in every part fit close to the funnel. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In cases where the contents of the filter require washing, the paper must not project over the rim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but also to prevent the solid particles being carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially such as are dissolved by acids, as sesquioxide of iron and lime. The common filtering paper of commerce seldom comes up to our requirements in this respect, and I would therefore always recommend to wash it with acid and water whenever it is intended for use in *accurate analyses*. For this purpose the apparatus shown in the figure will be found convenient. A is a bottle with the

Fig. 1.

bottom out, *a* and *b* are glass plates, between them lie the filters which have been previously cut and folded, *d* is a glass tube fitted into the cork *c*, *e* is a piece of flexible tube, which is closed by a piece of glass rod or a clip. The bottle is filled with a mixture of one part hydrochloric acid sp. gr. 1·12 and two parts water, in which the filters are allowed to soak twelve hours, the acid being then run off and replaced by ordinary water. After an hour this is replaced by fresh water, and so on till the washings are barely acid. The washing is continued with distilled water till the washings are free from hydrochloric acid—that is, till they cease to give any turbidity when mixed with a few drops of solution of nitrate of silver. Finally, the filters are drained, turned out onto blotting paper, covered with the same, and dried in a sieve in a warm place. When we merely want to wash two or three filters, we place them in a funnel, as in filtering, one inside the other, moisten them with dilute hydrochloric or nitric acid, and after some time wash them well with distilled water. Filtering paper, to be considered good, must, besides being pure, also let fluids pass readily through, yet completely retain even the finest pulverulent precipitates, such as sulphate of baryta, oxalate of lime, &c. Where a paper satisfying these requirements cannot be readily procured it is advisable to keep two sorts, one of closer texture for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles.

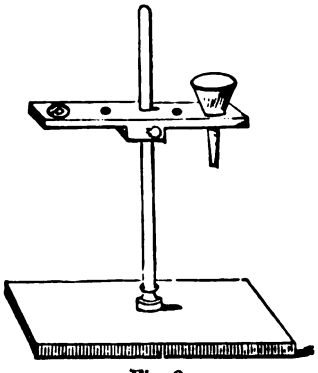

Fig. 2.

The funnels must be of glass or porcelain (§ 18, 10); they are usually placed on an appropriate stand, to keep them in a fixed position. The stand shown in fig. 2 is particularly well adapted for the reception of the small-sized funnels used in qualitative analyses.

The method of rapid filtration by means of an exhausting apparatus will be described in the *Quantitative Analysis*.

## § 6.

### 5. Decantation.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; as they will in such cases speedily subside to the bottom, thereby rendering it easy either to decant the supernatant fluid by simply inclining the vessel, or to draw it off by means of a syphon or pipette. In many cases we are obliged to employ decantation for the complete separation of precipitates from fluids, especially when a precipitate is of so gelatinous or slimy a nature that it would immediately stop the pores of a filter and prevent the passage of the fluid. Occasionally we combine decantation and filtration together by allowing the precipitate to settle, and then pouring the fluid as clear as possible onto a filter.

## § 7.

### 6. Washing.

In cases where filtration or decantation are resorted to for the purpose of obtaining the solid substance, the latter has to be freed afterwards by repeated washing from the liquid still adhering to it. The washing of precipitates collected on a filter is usually effected by means of the washing-bottle (fig. 3).

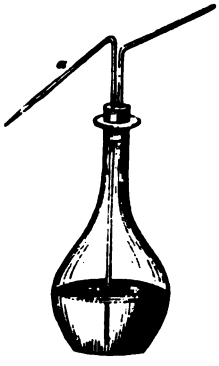

Fig. 3.

The drawing needs no elaborate explanation. The outer end of the tube *a* is drawn out to a fine point. By blowing air into the flask through the other tube, a fine jet of water is expelled through *a*, with a certain degree of force, which is particularly well suited for washing precipitates. Washing-bottles of this construction afford also the advantage that they do equally well for washing with hot water. For this purpose they are either furnished with a handle, or some cork is bound round the neck. The best way of washing by decantation is, after the supernatant fluid has been poured off, to stir up the precipitate with water or whatever fluid may be used for the washing, to allow to settle, to pour off again, and so on.

As the success of an analytical operation often depends absolutely upon the proper washing of a precipitate, it may as well be mentioned at once that the operation ought never to be considered completed before the object of it has been really attained. And this is usually the case only when the precipitate has been absolutely freed from the fluid adhering to it. The operator should, in this respect, never trust to mere belief or guessing, but should always make quite sure by properly testing the last washings. With fixed bodies it generally suffices to slowly evaporate a drop of the last washings on platinum-foil, when complete volatilization will show that the end in view has been fully attained.

## § 8.

### 7. Dialysis.

Dialysis is an operation which is occasionally employed for the separation of certain bodies from each other when they are in solution together; at first sight it appears to have some resemblance to filtration, but in reality it differs essentially from filtration. This operation has been recently introduced to the scientific world by Graham (Phil. Mag. Fourth Series, Nos. 153—155), and depends upon the different behaviour of bodies dissolved in water towards moist membranes. A certain class of bodies, the crystalloids, have the power of penetrating suitable membranes with which their solution may be placed in contact; whilst another class, the colloids, do not possess that property. Hence the two classes may be separated by taking advantage of this action. To the crystalloids belong all crystallizable bodies;

to the colloids all non-crystallizable bodies, as gelatine, gum, dextrin, caramel, tannin, albumen, extractive matters, hydrated silicic acid, &c. The septum must consist of a colloid material, as for instance an animal membrane, or, better still, parchment paper, and it must on the other side be in contact with water. GRAHAM explains the action on the assumption that the crystalloids appropriate to themselves the water absorbed by the colloid septum, acquiring thereby a medium for diffusion, whilst the dissolved colloids are unable to separate the water from the septum, and fail therefore to penetrate the latter. Figs. 4 and 5 exhibit suitable forms of apparatus for this opera-

Fig. 4.

Fig. 5.

tion. In fig. 4 the dialyser consists of the top of a bottle closed below with parchment paper; in fig. 5 it consists of a hoop covered like a sieve with parchment paper. The hoop may be of wood, or better of gutta-percha. The disk of parchment paper used should measure three or four inches in diameter more than the space to be covered; it is moistened, stretched over and fastened by a string or by an elastic band, but it should not be secured too firmly. The parchment paper must not be porous; its soundness may be tested by sponging the upper side with water, and observing whether wet spots show on the other side. Defects may be remedied by applying liquid albumen and coagulating this by heat. When the dialyser has thus been got ready, the mass to be examined is poured into it. If the mass is quite fluid the apparatus fig. 4 may be used, but if it contains undissolved solid matter, the hoop is to be preferred. The depth of fluid in the dialyser should not be more than half an inch, and the membrane should dip a little way below the surface of the water in the outer vessel, which should amount to at least four times the quantity of the fluid to be dialysed. The dialyser in fig. 4 is suspended in the manner indicated—the hoop is simply floated on the water. After twenty-four hours half or three-fourths of the crystalloids will be found in the external water, while the colloids remain in the dialyser—at most only traces pass into the external fluid. If the dialyser is brought successively in contact with fresh supplies of water, the whole of the crystalloids may be finally separated from the colloids. This operation is often of considerable service in chemico-legal

investigations for the extraction of poisonous crystalloids from parts of a dead body, food, vomit, &c.

There are four operations which serve to separate volatile substances from less volatile or from fixed bodies, viz., *evaporation*, *distillation*, *ignition*, and *sublimation*. The two former of these operations refer exclusively to fluids, the two latter exclusively to solids.

## § 9.

### 8. Evaporation

This is one of the most common operations in analytical chemistry. It serves to separate volatile fluids from less volatile or from fixed bodies (no matter whether solid or fluid), in cases where the residuary substance alone is of importance, whilst the evaporating matter is entirely disregarded;—thus, for instance, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to bring about crystallization of the salt; we resort to this process also for the purpose of removing the whole of the water from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form, &c. The evaporated water is entirely disregarded in either of these cases, the only object in view being to obtain, in the former case a more concentrated fluid, and in the latter a dry substance. These objects are invariably attained by converting the fluid which is to be removed to the gaseous state. This is generally done by the application of heat; sometimes also by leaving the fluid for a certain time in contact with the atmosphere, or with an enclosed volume of air constantly kept dry by hygroscopic substances, such as concentrated sulphuric acid, chloride of calcium, &c.; or, lastly, in many cases, by placing the fluid in rarefied air, with simultaneous application of hygroscopic substances. As it is of the utmost importance in qualitative analyses to guard against the least contamination, and as an evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted with proper expedition, in porcelain or platinum dishes, over the flame of a spirit or gas-lamp, in a separate place free from dust, preferably in a cupboard provided with a draught. If the operator has no place of the kind, he must have recourse to the much less suitable proceeding of covering the dish; the best way of doing this is to place over the dish a large glass funnel secured by a retort-holder, in a manner to leave sufficient space between the rim of the funnel and the border of the dish; the funnel is placed slightly aslant, that the drops running down its sides may be received in a beaker. Or the dish may also be covered with a sheet of filter-paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid (see § 5); were common and unwashed filter-paper used for the purpose, the sesquioxide of iron, lime, &c., contained in it would dissolve in the vapors evolved (more especially if acid), and the solution dripping down into the evaporating fluid would speedily contaminate it. These precautions are necessary of course only in accurate analyses. Large quantities of fluid are evaporated best in flasks standing aslant, covered with a cap of pure filtering paper, over a charcoal fire or gas; or also in tubulated retorts with neck rising

obliquely upward, and open tubulure. Evaporating processes at 100° are conducted in a suitable steam apparatus, or in the water-bath shown in fig. 6. Evaporation to dryness is not usually conducted over the naked flame, but generally either on the water-bath or the sand-bath, or on an iron plate.

Fig. 6.

There is a circumstance connected with the subject which should be noted here; namely, that porcelain and glass vessels—which we can hardly avoid using for the evaporation of large quantities of fluids—are slightly attacked, and so their contents become more or less contaminated with their constituents. This will be more fully discussed in the *Quantitative Analysis*, but it becomes a source of great trouble in delicate work. I will now be content to advise the student never to evaporate alkaline fluids in glass, as at a boiling temperature they attack it considerably.

## § 10.

### 9. Distillation.

This operation serves to separate a volatile liquid from a less volatile or a non-volatile substance (no matter whether solid or fluid) where the object is to recover the evaporating fluid. In order to attain this end, it is necessary to reconvert the liquid from the gaseous form in which it evaporates into the fluid state. A distilling apparatus consists consequently always of three parts, no matter whether separable or not. These three parts are—1st, a vessel in which the liquid to be distilled

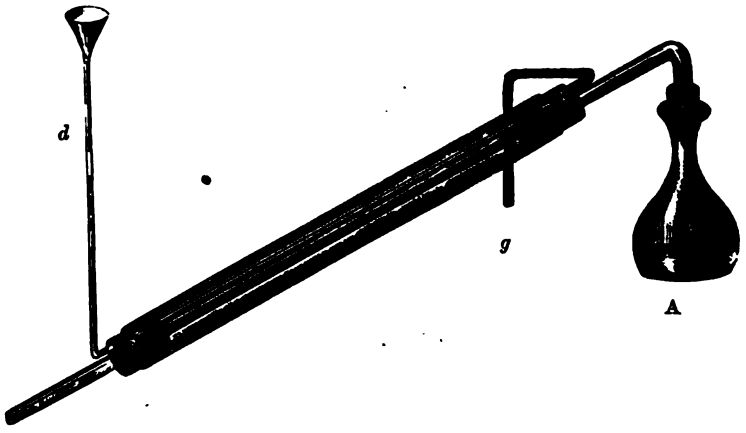

Fig. 7.

is heated, and thus converted into vapor; 2nd, an apparatus in which this vapor is cooled again or condensed, and thus reconverted to the fluid state; and 3rd, a vessel to receive the fluid thus reproduced by the condensation of the vapor (the distillate). For the distillation of large quantities metallic apparatus are used (copper stills with head and condenser of tin), or large glass retorts; in analytical investigations we either use small retorts with receivers, or more usually an apparatus such

as is shown in fig. 7. The fluid to be distilled is boiled in A, and the vapor escapes through the tube which is fitted into the cork. The tube is surrounded with a wider tube which is filled with cold water. In proportion as the water cools the inner tube, it becomes heated itself, and consequently requires renewing continually or occasionally, which is done by pouring cold water in through *d*, after placing a vessel under *g* to catch the hot water which will run out. A small flask serves as a receiver.

## § 11.

### 10. Ignition.

Ignition is, in a certain manner, for solid bodies what evaporation is with regard to fluids; since it serves (at least generally) to separate volatile substances from less volatile or from fixed bodies in cases where the residuary substance alone is of importance. The process of ignition always presupposes the application of a high temperature, in which respect it differs from drying. The form or state which the eliminated substance assumes on cooling—whether it remains gaseous, as in the ignition of carbonate of lime; or assumes the liquid state, as in the ignition of hydrate of lime; or solidifies, as in the ignition of a mixture containing chloride of ammonium—is a matter of perfect indifference as regards the name given to the operation.

The process of ignition is mostly employed, as has just been said, to effect the elimination of a volatile body. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus the sesquioxide of chromium is converted by ignition into the so-called insoluble modification, &c. In analytical investigations substances under examination are often ignited also, that the operator may from their deportment at a red heat draw a conclusion as to their nature in general, their fixity, their fusibility, the presence or absence of organic matter, &c.

Crucibles are the vessels generally made use of in ignition. In operations on a large scale Hessian or black-lead crucibles are used, heated by charcoal or gas; in analytical experiments small-sized crucibles or dishes are selected, of porcelain, platinum, silver, or iron, or glass tubes sealed at one end, according to the nature of the substances to be ignited; these crucibles, dishes, or tubes are heated over a Berzelius spirit-lamp, or a gas-lamp, or a bellows blowpipe.

## § 12.

### 11. Sublimation.

The term *sublimation* designates the process which serves to convert solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration;—the substance volatilized and recondensed is called a *sublimate*. Sublimation is consequently a distillation of solid bodies. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of volatility. Its application is of the highest importance in analysis for the detection of certain substances, *e.g.* of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of *volatility* of the substances operated upon. In

sublimations for analytical purposes we generally employ sealed glass tubes. When the sublimation is performed with the aid of a current of hydrogen or carbonic acid we use open glass tubes, which are usually made narrower just behind the part to which the heat is applied.

## § 13.

### 12. Fusion.

Simple fusion is the conversion of a solid substance into the fluid form by the application of heat; it is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term is also applied in cases where substances insoluble or difficult of solution in water and acids are by fusion in conjunction with some other body modified or decomposed in such a manner that they or the new-formed compounds will subsequently dissolve in water or acids. Fusion is conducted either in porcelain, silver, or platinum crucibles, according to the nature of the compound. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the iron ring of the Berzelius spirit-lamp or the gas-lamp. Triangles of thick iron wire, especially when laid upon the stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures. Small quantities of matter are also often fused in glass tubes sealed at one end.

Resort to fusing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates and alumina compounds. The flux most commonly used is carbonate of soda or carbonate of potassa, or, better still, a mixture of both in equal atomic proportions (see § 76). In certain cases hydrate of baryta is used instead of the alkaline carbonates.

For the fusion of aluminates, bisulphate of potassa or bisulphate of soda is frequently used.

A platinum crucible is used for the fusion, whether alkaline carbonates, hydrate of baryta, or alkaline bisulphates are employed.

I have to add here a few precautionary rules for the prevention of damage to the platinum vessels used in these operations. No substance evolving chlorine ought to be treated in platinum vessels; no nitrates of the alkalies, hydrate of potassa and soda, metals, or sulphides of metals or cyanides of the alkali metals should be fused in such vessels; nor should readily deoxidizable metallic oxides, or salts of the heavy metals with organic acids be ignited in them, or phosphates in presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them direct to an intense charcoal fire, as the action of the ash is likely to lead to the formation of silicide of platinum, which renders the vessel brittle. It is always advisable to support platinum crucibles used in ignition or fusion on triangles of platinum wire. When a platinum crucible has been made white hot over the bellows blowpipe, it is unwise to cool it too quickly by suddenly turning off the gas, and allowing the cold blast to play upon it, since the crucible is under these circumstances very liable to become slightly cracked. Platinum crucibles are cleaned by rubbing with wet sea-sand, the round grains of which do not scratch the metal. Where this fails to remove the stains the desired object may be attained by

fusing bisulphate of potassa or borax in the crucible, boiling subsequently with water, and polishing finally with sea-sand.

We have still to speak here of another operation which bears some affinity to fusion, viz.—

## § 14.

### 13. Deflagration.

We understand by the term *deflagration*, in a more general sense, every process of decomposition attended with noise or detonation—the cause of the decomposition being a matter of perfect indifference as regards the application of the term in this sense. We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another substance mixed with it (usually a nitrate or a chlorate), and connect with it the idea of a sudden and violent combustion attended with vivid incandescence and noise or detonation.

Deflagration is resorted to either to produce the desired oxide—thus sulphide of arsenic is deflagrated with nitrate of potassa to obtain arsenate of potassa; or it is applied as a means to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid by fusing them with cyanide of potassium, and observing whether they deflagrate, &c. To attain the former object the perfectly dry mixture of the substance and the deflagrating agent is projected in small portions at a time into a red-hot crucible. Experiments of the latter description are invariably made with minute quantities preferably on a piece of thin platinum foil, or in a small spoon.

## § 15.

### 14. The Use of the Blowpipe.

This operation belongs exclusively to the province of analytical chemistry, and is of paramount importance in many analytical processes. We have to examine here the apparatus required, the mode of its application, and the results of the operation.

The blowpipe fig. 8 is a small instrument, usually made of brass or German silver. It was originally used for soldering, whence it derived the name of *soldering pipe* (*Löthrohr*), by which the Germans designate it. It consists of three distinct parts; viz., 1st, a tube *a b*, fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth; 2nd, a small cylindrical vessel *c d*, into which *a b* is screwed air-tight, and which serves as an air-chamber and to retain the moisture of the air blown into the tube; and 3rd, a smaller tube *f g*, also fitted into *c d*. This small tube, which forms a right angle with the larger one, is fitted at its aperture either simply with a finely perforated platinum plate, or more conveniently with a finely perforated platinum cap (*h*). The construction of the cap is shown in fig. 9. It is,

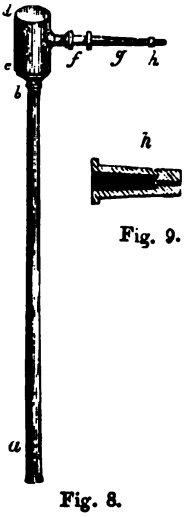

Fig. 8.



Fig. 9.

indeed, a little dearer than a simple plate, but it is also much more durable. If the opening of the cap gets stopped up, the obstruction may generally be removed by heating it to redness before the blowpipe.

The proper length of the blowpipe depends upon the distance to which the operator can see with distinctness; it is usually from twenty to twenty-five centimetres. The form of the mouthpiece varies. Some chemists like it of a shape to be encircled by the lips; others prefer the form of a trumpet mouthpiece, which is only pressed against the lips. The latter requires less exertion on the part of the operator, and is accordingly generally chosen by those who have a great deal of blowpipe work.

Fig. 10.

The blowpipe serves to conduct a continuous fine current of air into a gas-flame, or into the flame of a candle or lamp, or sometimes into a spirit-of-wine flame. The flame of a candle (and equally so that of gas or of an oil lamp), burning under ordinary circumstances, is seen to consist of three distinct parts, as shown in fig. 10, viz., 1st, a dark nucleus in the centre (*a*); 2nd, a luminous cone surrounding this nucleus (*efg*); and, 3rd, a feebly luminous mantle encircling the whole flame (*bcd*). The dark nucleus is formed by the gases which the heat evolves from the wax or fat, and which cannot burn here for want of oxygen. In the luminous cone these gases come in contact with a certain amount of air insufficient for their complete combustion. In this part, therefore, it is principally the hydrogen of the carbides of hydrogen evolved which burns, whilst the carbon separates in a state of intense ignition, which imparts to the flame the luminous appearance observed in this part. In the outer coat the access of air is no longer limited, and all the matter not yet burned is consumed here. This part of the flame is the hottest, and the extreme apex is the hottest point of it. Oxidizable bodies oxidize therefore with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, viz. high temperature and an unlimited supply of oxygen. This outer part of the flame is therefore called the *oxidizing flame*. On the other hand, oxides having a tendency to yield up their oxygen suffer reduction when placed within the luminous part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed carbide of hydrogen there present. The luminous part of the flame is therefore called the *reducing flame*.

Now the effect of blowing a fine stream of air across a flame is, first, to alter the shape of the flame, as, from tending upward, it is now driven sideways in the direction of the blast, being at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase of the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the blast will depend upon whether the operator wants a reducing or an oxidizing flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a jet, shaped as in fig. 11, the slit being 1 centimetre long and 1½ to 2 millimetres wide; as with the

use of gas the operator is enabled to regulate not only the current of air, but that of the gas also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some moveable metallic support, such as, for instance, the ring of BUNSEN'S gas-lamp intended for supporting dishes, &c.

Fig. 11 shows the flame for reducing, fig. 12 the flame for oxidizing. The luminous parts are shaded.

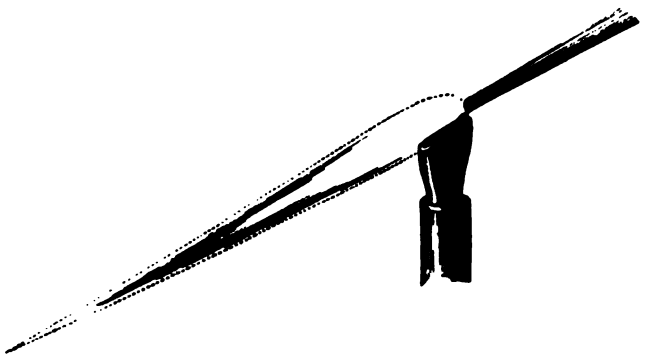

Fig. 11.

The *reducing flame* is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the *oxidizing flame*, the gas is lowered, the jet

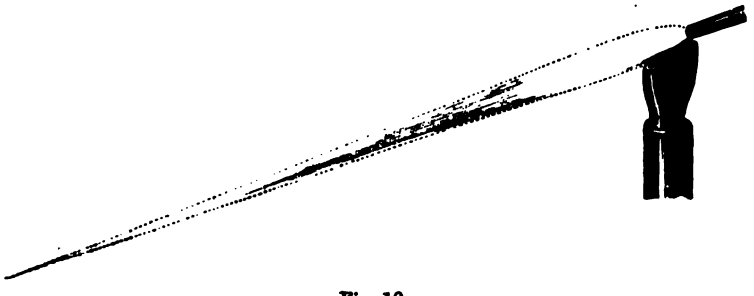

Fig. 12.

of the blowpipe pushed a little further into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas, and an inner pointed, bluish cone, slightly luminous towards the apex is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect their fusion; but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion.

An oil-lamp with broad wick of proper thickness may be used instead of gas; a thick wax-candle also will do. For an oxidizing flame a small spirit-lamp will in most cases answer the purpose.

The *current* is produced with the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe quietly with distended cheeks and with the blowpipe between the lips; with practice and patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

*Charcoal supports* are used principally in the reduction of metallic oxides, &c., or in trying the fusibility of bodies. The substances to be operated upon are put into small conical cavities, scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic fumes are re-oxidized, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colors, leading to the detection of the metals. Thoroughly-burnt pieces of charcoal only should be selected, otherwise they are apt to spirt and throw off the substance. The charcoal of the wood of the pine, linden, or willow, is greatly preferable to that of harder woods, and woods which are richer in ash. Smooth pieces ought to be selected, as knotty pieces are apt to spirt when heated, and to throw off the substance. The most convenient way is to saw the charcoal of well-seasoned and straight-split pinewood into parallelo-pipedic pieces, and to blow or brush off the dust; they may then be handled without soiling the hands. Those sides alone are used on which the annual rings are visible on the edge, as on the other sides the fused matters are apt to spread over the surface of the charcoal (Berzelius). Small charcoal supports are sometimes sold, which have been made from powdered charcoal, mixed with rice or starch paste, and stamped into convenient shapes—they are very handy and clean.

The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—1st, its infusibility; 2nd, its low conducting power for heat, which permits substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, which makes it imbibe readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on the surface; 4th, its reducing power, which greatly contributes to the reduction of oxides in the inner blowpipe flame.

We use *platinum wire*, and occasionally also *platinum foil*, in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them and to watch the phenomena attending the solution, and mark the color of the bead; lastly, also to introduce substances into the flame, to see whether they will color it. The wire is cut into lengths of 8 centimetres, and each

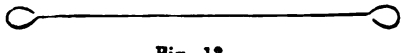

Fig. 13.

length twisted at both ends into a small loop (fig. 13). When required for use, the loop is moistened with a drop of water, then dipped into

the powdered flux (where a flux is used), and the portion adhering fused in the flame of a gas- or spirit-lamp. When the bead produced, which sticks to the loop, is cold, it is moistened again, and a small portion of the substance to be examined put on and made to adhere to it by the action of a gentle heat. The loop is then finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

What renders the application of the blowpipe particularly useful in chemical experiments is the great expedition with which the intended results are attained. These results are of a twofold kind, viz., either they afford us simply an insight into the general properties of the body, and enable us accordingly only to determine whether it is fixed, volatile, fusible, &c.; or the phenomena which we observe enable us at once to recognise the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the different substances with reagents.

As in the use of the blowpipe one hand is always necessarily engaged, and the production of a continued blast requires practice and some slight exertion, and as, lastly, it is not very easy to maintain the blowpipe flame always steadfastly, so that the substances exposed to it are undeviatingly kept in the desired parts of the flame, many chemists have long been endeavouring to devise some self-acting blowpipe apparatus, and many contrivances of the kind have been proposed and have found favour. In some of them the air-current is produced by means of a gasometer, in others by means of a caoutchouc balloon, in others again by a species of hydrostatic blast, &c. But the simplest self-acting blowpipe apparatus, by which most of the objects attainable with the blowpipe may be most suitably and conveniently accomplished, is the Bunsen gas-lamp, provided with a chimney, which burns without luminosity and without soot. A description of this lamp follows in the next paragraph.

## § 16.

### 15. The Use of Lamps, particularly of Gas-lamps.

As we have to deal mostly with smaller quantities of matter only, we use in processes of qualitative analysis requiring the application of heat, such as evaporation, distillation, ignition, &c., generally lamps, either spirit-lamps or, where coal-gas is obtainable, most advantageously, gas-lamps.

Of *spirit-lamps* there are two kinds in use, viz., the simple spirit-lamp, as shown in fig. 16, and the Berzelius lamp with double draught (fig. 14). In the construction of the latter lamp it should be borne in mind that the part containing the wick and the vessel with the spirit must be in separate pieces, connected only by means of a narrow tube; otherwise troublesome explosions are apt to occur in lighting the lamp. Nor should the chimney be too narrow, or the stopper fit air-tight on the mouth through which the spirit is poured in. A lamp should be selected that may be readily moved up and down the pillar of the stand, which must be fitted with a moveable brass ring to support dishes and flasks in processes of ebullition, and a ring of moderately stout iron wire to support the triangle for holding the crucibles in the processes of ignition and fusion. Of the various forms of lamps in use, the one shown

in fig. 14 is the most suitable and elegant. Fig. 15 shows a triangle of platinum wire fixed within an iron wire ring; this serves to support the crucible in processes of ignition. Glass vessels, more particularly

Fig. 14.

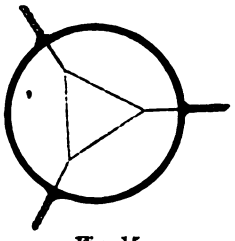

Fig. 15.

Fig. 16.

beakers, which it is intended to heat over the lamp, are most conveniently rested on a piece of gauze made of fine iron wire such as is used in making sieves of medium fineness.

Of the many *gas-lamps* proposed, BUNSEN'S, as shown in its simplest form in figs. 17 and 18, is the most convenient. *a b* is a foot of cast iron measuring 7 cm. in diameter. In the centre of this is fixed a square brass box, *c d*, which slightly tapers towards the top; the sides of this box are 25 mm. high, and 16 mm. wide; it has a cylindrical cavity of 12 mm. deep, and 10 mm. in diameter. Each side of the box has, 4 mm. from the upper rim, a circular aperture of 8 mm. diameter, leading to the inner cavity. One of the sides has fitted into it, 1 mm. below the circular aperture, a brass tube, which serves for the attachment of the India-rubber supply tube. This brass tube is turned in the shape shown in fig. 17; it has a bore of 4 mm. The gas conveyed into it re-issues from a tube in the centre of the cavity of the box. This tube, which is 4 mm. thick at the top, thicker at the lower end, projects 3 mm. above the rim of the box; the gas issues from a narrow opening which appears formed of 3 radii of a circle, inclined to each other at an angle of 120°. The length of each radius is 1 mm.; the opening of the slit is $\frac{1}{8}$ mm. wide; *e f* is a brass tube 95 mm. long, open at both ends, with a bore of 9 mm.; the screw at the lower end of this tube fits into the upper part of the cavity of the box. With this tube screwed in, the lamp is completed. On opening the stop-cock, the gas rushes into the tube *e f*, where it mixes with the air coming in through the circular apertures. When this mixture is kindled at *f*, it burns with a straight, upright, bluish flame, entirely free from soot, which may be regulated at will by opening the stop-cock more or less; a partial opening of the cock suffices to give a flame fully answering the purpose of

the common spirit-lamp; whilst with the full stream of gas turned on, the flame, which will now rise up to 2 decimetres in height, affords a most excellent substitute for the Berzelius lamp. If the flame is made to burn very low, it will often occur that it recedes; in other words, that instead of the mixture of gas and air burning at the mouth of the tube *e f*, the gas takes fire on issuing from the slit, and burns below in the tube. This defect may be perfectly obviated by covering the tube *e f* at the top with a little wire gauze cap. Flasks, &c., which it is intended

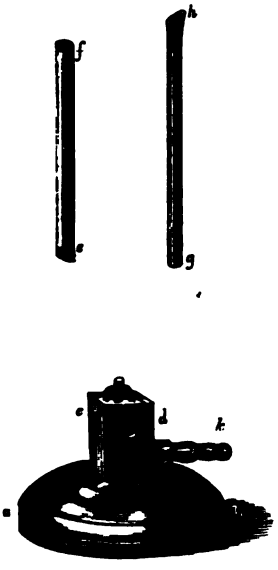


Fig. 17.

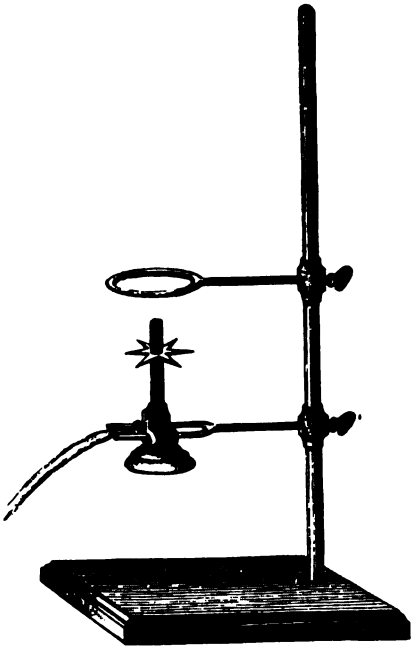

Fig. 18.

to heat over the gas-lamp, are most conveniently supported on a gauze-plate. We give this name to a square piece of thin iron plate to which a piece of wire gauze of equal size is riveted, as shown in fig. 19. We can also use simple wire gauze, but this rapidly burns through in the middle, and does not offer the same protection against the cracking of beakers or flasks. If it is wished to use the gas-lamp for blowpipe operations, the tube *g h* must be inserted into *e f*; this tube terminates in a flattened top slanting at an angle of 68° to the axis, and having an opening in it 1 cm. long, and 1½ to 2 mm. wide. The insertion of *g h* into *e f* serves to close up the air-holes in the box, and pure gas, burning with a luminous flame, issues accordingly now from the top of the tube. Fig. 18 shows the apparatus complete, fixed in the fork of an iron stand; this arrangement *permits the lamp* being moved backward and forward

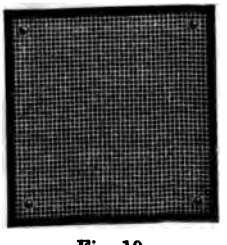

Fig. 19.

between the prongs of the fork, and up and down the pillar of the stand. The moveable ring on the same pillar serves to support the objects to be operated upon. The 6 radii round the tube of the lamp serve to support an iron-plate chimney (see fig. 23), or a porcelain plate used in quantitative analyses.

Fig. 20.

To heat crucibles to the brightest red heat, or to a white heat, the *bellows blowpipe* is resorted to. But even without this the action of the gas-lamp may be considerably heightened by heating the crucible within a small clay furnace, as recommended by O. L. ERDMANN. Fig. 20 shows the simple contrivance by which this is effected. The furnaces are 115 mm. high, and measure 70 mm. diameter in the clear. The thickness of material is 8 mm. If the ordinary Bunsen burner is not sufficiently strong for any purpose, the three-Bunsen burner (fig. 21) may be used.

BUNSEN has devised a more perfect form of this lamp* to render the flame a more complete substitute for the blowpipe flame, namely, for reducing,

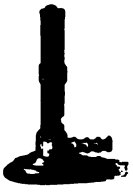

Fig. 21.

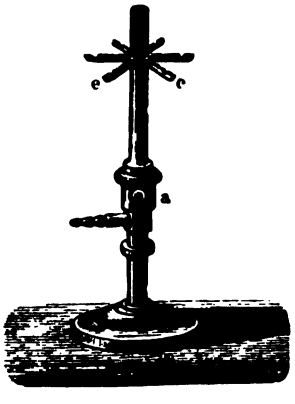


Fig. 22.

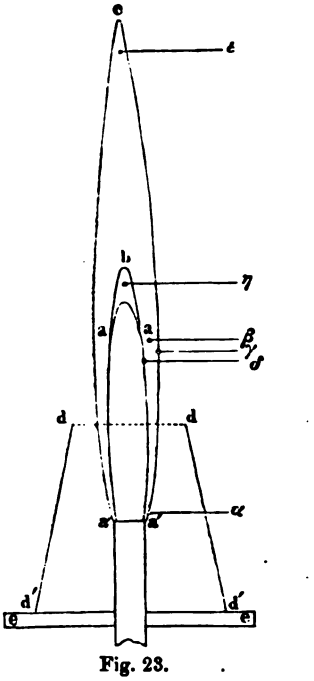


Fig. 23.

oxidizing, fusing, and volatilizing, and for the observation of the coloration of flame (§ 17). This improved form of the lamp is

* Annal. d. Chem. u. Pharm., 111, 257 and 138, 257. Also Zeitschr. f. anal. Chem., 5, 351.

shown in fig. 22, *a* is a sheath, which can be turned round for regulating the flow of air. When in use the conical chimney *d d d d* (fig. 23) is placed on *e e*, it is of such dimensions that the flame may burn tranquilly. Fig. 23 shows the flame half its natural size. In this three parts are at once apparent, namely, 1. *a a a a* the dark cone, which contains the cold gas mixed with about 62 per cent. of air, 2. *a c a b* the mantle formed by the burning mixture of gas and air, 3. *a b a* the luminous tip of the dark cone, which does not appear unless the air-holes are somewhat closed. The latter is useful for reductions.

Such are the three principal parts of the flame, but BUNSEN distinguishes no less than six parts, which he names as follows.

1. *The base* at *a*, which has a relatively low temperature, because the burning gas is here cooled by the constant current of fresh air, and also because the lamp itself conducts the heat away. This part of the flame serves for discovering the colors produced by readily volatile bodies when less volatile bodies which color the flame are also present. At the relatively low temperature of this part of the flame the former volatilize alone instantaneously, and the resulting color imparted to the flame is for a moment visible unmixed with other colors.

2. *The fusing zone.* This lies at $\beta$, at a distance from the bottom of somewhat more than one-third of the height of the flame, equidistant from the outside and the inside of the mantle, which is broadest at this part. This is the hottest part of the flame, namely, about 2300°, and it therefore serves for testing substances as to their fusibility, volatility, emission of light, and for all processes of fusion at a high temperature.

3. *The lower oxidizing zone* lies in the outer border of the fusing zone at $\gamma$, and is especially suitable for the oxidation of oxides dissolved in vitreous fluxes.

4. *The upper oxidizing flame* at $\varepsilon$ consists of the non-luminous tip of the flame. Its action is strongest when the air-holes of the lamp are fully open. It is used for the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at $\delta$ in the inner border of the fusing zone next to the dark cone. The reducing gases are here mixed with oxygen, and therefore do not possess their full power, hence they are without action on many substances which are deoxidized in the upper reducing flame. This part of the flame is especially suited for reduction on charcoal or in vitreous fluxes.

6. *The upper reducing flame* lies at $\eta$ in the luminous tip of the dark inner cone, which, as I have already explained, may be produced by diminishing the supply of air. This part of the flame must not be allowed to get large enough to blacken a test-tube filled with water and held in it. It contains no free oxygen, is rich in separated incandescent carbon, and therefore has a much stronger action than the lower reducing zone. It is used more particularly for the reduction of metals collected in the form of incrustations.

With the help of a gas flame of this description we can obtain as high a temperature as with the blowpipe, and even higher if the radiating surface of the substance is made as small as possible; and by the use of the different parts of the flame processes of reduction and of oxidation may be carried out with the greatest convenience.

In order to study *the deportment of bodies at a high temperature*, namely,

their emission of light, fusibility, volatility and power of coloring flame, they are introduced into the flame in the loop of a platinum wire, which should be barely thicker than a horse hair. Should the substance attack platinum, a little bundle of asbestos is used, which should be about one-fourth the thickness of a match. Decrepitating substances are first very finely powdered, then placed on a strip of moistened filter-paper about a square centimetre in surface, and this is cautiously burnt between two rings of fine platinum wire. The substance now presents the appearance of a coherent crust and may be held in the flame without difficulty. For testing fluids to see whether they contain a substance which colors flame, the round loop of the fine platinum wire is flattened on an anvil to the form of a small ring. This is dipped into the fluid, and then withdrawn, when a drop will be found attached to the ring. This drop is held near the flame and allowed to evaporate without boiling, after which the residue may be conveniently tested.

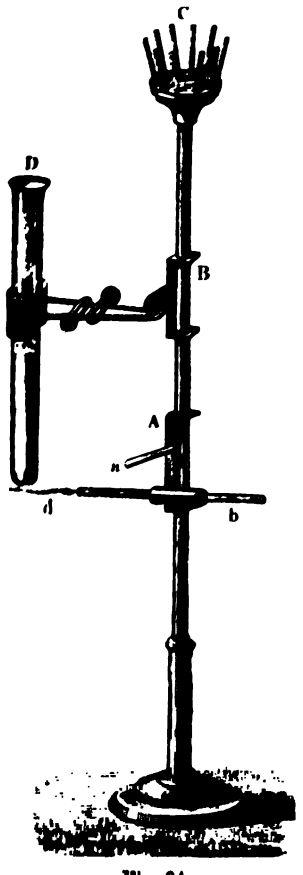

Fig. 24.

If bodies are to be exposed for a considerable time to the action of the flame, the stand, fig. 24, is used. *A* and *B* are provided with springs, and can be easily moved up and down. On *A* is the arm *a* intended for the support of the platinum wire fixed in a glass tube (fig. 25); also another little arrangement to hold the glass tube *b* with its bundle of asbestos fibres *d*. *B* bears a clip for the reception of a test tube, which in certain cases has to be heated for a considerable time in a definite part of the flame. *C* serves to hold the various platinum wires fixed in glass tubes.

Fig. 25.

*Experiments of reduction* are performed either with the aid of a suitable reducing agent in a small glass tube, or with the aid of a little stick of charcoal. In order to prepare the latter, BUNSEN recommends to hold an uneffloresced crystal of carbonate of soda near the flame, and then having taken off the head of a match to smear three-fourths of its length with the wet mass produced by warming the crystal. The match is then slowly rotated on its axis in the flame, when a crust of solid carbonate of soda will form on the carbonized wood, and on heating in the fusing zone of the flame this crust will be melted and absorbed by the charcoal. The little stick of charcoal will now in a measure be protected from combustion. The substance to be tested is made into a

paste, with a drop of melted crystallized carbonate of soda, and a mass about the size of a millet-seed is taken up on the point of the carbonized match, it is then first melted in the lower oxidizing flame, and afterwards moved through a portion of the dark cone into the opposite hottest part of the lower reducing zone. The reduction will be rendered evident by the effervescence of the carbonate of soda. After a few moments the action is stopped by allowing the substance to cool in the dark cone of the flame. If, finally, the point of the carbonized match is cut off and triturated with a few drops of water in a small agate mortar, the reduced metal will be obtained in the form of sparkling fragments which may be purified by elutriation, and if necessary more minutely examined.

Volatile elements which are reducible by hydrogen and carbon may be separated as such or as oxides from their combinations and deposited on porcelain. These deposits are called *incrustations*, they are thicker in the middle, and become thin towards the edges. They may be converted into iodides, sulphides, and other combinations, and may thus be further identified. These reactions are so delicate that in many cases a quantity of from $\frac{1}{10}$ to 1 mgrm. is sufficient to exhibit them.

*The metallic incrustation* is obtained by holding in one hand a small portion of the substance on asbestos in the upper reducing flame, and in the other hand a glazed porcelain dish, from 1 to 1·2 decimetres in diameter, filled with water, close over the asbestos in the upper reducing flame. The metals separate as sooty or mirror-like incrustations.

If the substance is held as just directed, and the porcelain dish is held in the upper oxidizing flame then an *incrustation of oxide* is obtained. In order to be sure of getting it, the flame must be comparatively small if the portion of substance is minute. To turn the incrustation of oxide into an *incrustation of iodide*, let the dish covered with the oxide cool, breathe on it, and place it on the wide-mouthed bottle, fig. 26. This bottle contains iodide of phosphorus, which has been allowed to deliquesce and become converted into fuming hydriodic acid and phosphorous acid, it should have an air-tight glass stopper. If the hydriodic acid has become so moist that it has ceased to fume it may be restored to its proper condition by the addition of anhydrous phosphoric acid. To turn the incrustation of iodide into an *incrustation of sulphide*, direct a current of air containing sulphide of ammonium upon it, breathing upon the dish occasionally, then drive off the excess of sulphide of ammonium by *gentle* warming.

Fig. 26.

If more considerable quantities of the metallic incrustation are required for further experiments, the porcelain dish is replaced by a test-tube half filled with water (*D*, fig. 24), in which a few pieces of marble should be placed to prevent bumping when the water is subsequently boiled. In this case the asbestos (*d*) with the substance on it is fixed at the same height as the middle of the upper reducing flame, the test-tube is fixed with its bottom just over the asbestos as shown in the figure, and then the lamp is moved just under the test-tube. The substance thus comes within the *reducing flame* and the metallic incrustation forms

on the bottom of the test-tube. The incrustation may be obtained as thick as is wished by renewal of the substance.

## § 17.

### [16. Observation of the Coloration of Flame and Spectrum Analysis.

Many substances have the property of coloring a colorless flame in a very remarkable manner. As most of these substances impart a different and distinct, and accordingly characteristic, tint to the flame, the observation of this colorization of flame affords an excellent, easy, and safe means of detecting many of these bodies. Thus, for instance, salts of soda impart to flame a yellow, salts of potassa a violet, salts of lithia a carmine tint, and may thus be easily distinguished from each other.

The flame of Bunsen's gas-lamp, with chimney, described in § 16, and shown in fig. 22, is more particularly suited for observations of the kind. The substances to be examined are put on the small loop of a fine platinum wire, and thus, by means of the holder shown in fig. 24, or the more simple one, fig. 27, placed in the fusing zone of the gas-flame. A particularly striking coloration is imparted to the flame by the salts of the alkalies and alkaline earths. If different salts of one and the same base are compared in this way, it is found that every one of them, if at all volatile at high temperatures, or permitting at least the volatilization of the base, imparts the same color to the flame, only with different degrees of intensity, the most volatile of the salts producing also the most intense coloration; thus, for instance, chloride of potassium gives a more intense coloration than carbonate of potassa, and this latter again a more intense one than silicate of potassa. In the case of difficultly volatile compounds, the coloration of the flame may often be brought about, or made more apparent, by adding some other body which has the power of decomposing the compound under examination. Thus, for instance, in silicates containing only a few percents of potassa, the latter body cannot be directly detected by coloration of flame; but this detection may be accomplished by adding a little pure gypsum, as this will cause formation of silicate of lime and sulphate of potassa, a salt which is sufficiently volatile.

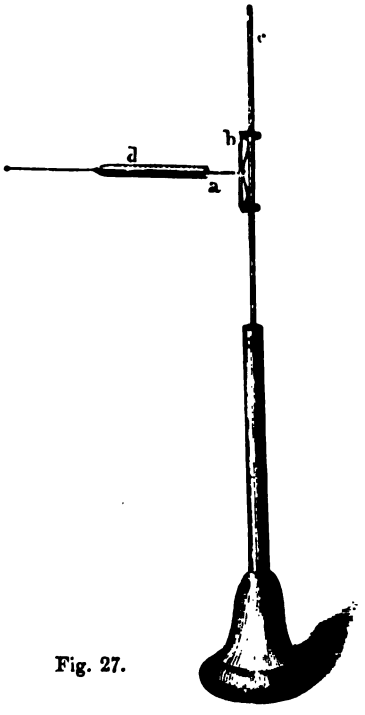


Fig. 27.

But however decisive a test the mere coloration of flame affords for the detection of certain metallic compounds, when present unmixed with others, this test becomes apparently quite useless in the case of mixtures of compounds of several metals. Thus, for instance, mixtures of salts of potassa and soda show only the soda flame, mixtures of salts of baryta and strontia only the baryta flame, &c. This defect may be remedied, however, in two ways, with the most surprising success. Both ways have only recently been discovered.

The *first way* introduced by CARTMELL,* and perfected afterwards by BUNSEN† and by MERZ,‡ consists in looking at the colored flame through some colored medium (colored glasses, indigo solution, &c.). Such colored media, in effacing the flame coloration of the one metal, bring out that of the other metal mixed with it. For instance, if a mixture of a salt of potassa and a salt of soda is exposed to the flame, the latter will only show the yellow soda coloration; but if the flame be now looked at through a deep-blue cobalt glass, or through solution of indigo, the yellow soda coloration will disappear and will be replaced by the violet potassa tint. A simple apparatus suffices for all observations and experiments of the kind; all that is required for the purpose being,—

1. A hollow prism (fig. 28) composed of mirror plates, the chief section of which forms a triangle with two sides of 150 mm., and one

Fig. 28.

side of 35 mm. length. The indigo solution required to fill this prism is prepared by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, adding to the solution 1500-2000 parts of water, and filtering. When using this apparatus, the prism is moved in a horizontal direction close before the eyes in such a way that the rays of the flame are made to penetrate successively thicker and thicker layers of the effacing medium.

2. A blue, a violet, a red, and a green glass. The blue glass is tinted with protoxide of cobalt; the violet glass with sesquioxide of manganese; the red glass (partly colored, partly uncolored) with suboxide of copper; and the green glass with sesquioxide of iron and protoxide of copper. The common colored glass will generally be found to answer the purpose. As regards the tints imparted to the flame by the different bodies, when viewed through the aforesaid media, and the combinations, by which these bodies are severally identified, the information required will be found in Section III., in the paragraphs treating of the several bases and acids.

The *second way*, which is called *Spectrum Analysis*, was introduced by KIRCHHOFF and BUNSEN. It consists in letting the rays of the colored flame pass first through a narrow slit, then through a prism, and observing the so refracted rays through a telescope. A distinct spectrum

* Phil. Mag., 16, 328. † Annal. d. Chem. u. Pharm., 111, 257.
‡ Journ. f. prakt. Chem., 80, 487.

is thus obtained for every flame-coloring metal: this spectrum consists either, as in the case of baryta, of a number of colored lines lying side by side; or, as in the case of lithia, of two separate, differently-colored lines; or, as in the case of thallium, of a single green line. These spectra are characteristic in a double sense—viz., the spectrum lines have a distinct color, and they occupy also a fixed position.

It is this latter circumstance which enables us to identify without difficulty, in the spectrum observation of mixtures of flame-coloring metals, every individual metal. Thus, for instance, a flame in which a mixture of potassa, soda, and lithia salts is evaporated, will give, side by side, the spectra of the several metals in the most perfect purity.

KIRCHHOFF and BUNSEN have constructed two kinds of apparatus, which are both of them suited for spectrum observation, and enable the operator to determine by measure the positions in which the spectrum lines make their appearance. Both are constructed upon the same principle. A description, with illustration, of the larger of the two, which is also the most perfect one, has been published in POGGENDORFF'S *Annalen*, 113, 374, and in the *Zeitschrift für Analytische Chemie*, 1862, 49. The smaller, more simple, and accordingly cheaper apparatus, which suffices for all common purposes, and is used most in chemical laboratories, we will describe here. It is shown in fig. 29 *a*.

Fig. 29 *b*.

Fig. 29 *a*.

*A* is an iron disk, in the centre of which a prism, with circular refracting faces of about 25 mm. diameter, is fastened by a bow, which presses upon the upper face of the prism, and is secured below to the iron plate by a screw. The same disk has also firmly fastened to it the three tubes *B*, *C*, and *D*. Each of these tubes is soldered to a metal block, of which fig. 29 *b* gives an enlarged representation. This block contains the nuts for two screws, which pass through wider openings in the iron plate, and are firmly secured beneath when the tube has been adjusted in the proper position. *B* is the observation telescope; it has

a magnifying power of about 6, with an object-glass of 20 mm. diameter. The tube *C* is closed at one end by a tin-foil disk, into which the perpendicular slit is cut through which the light is admitted.* The tube *D* carries a photographic copy of a millimetre-scale, produced in the camera obscura on a glass plate of about one-fifteenth the original dimensions. This scale is covered with tin-foil, with the exception of the narrow strip upon which the divisional lines and the numbers are engraved. It is lighted by a gas or candle-flame placed close behind it.

The axes of the tubes *B* and *D* are directed, at the same inclination, to the centre of one face of the prism, whilst the axis of the tube *C* is directed to the centre of the other face. This arrangement makes the spectra produced by the refraction of the colored light passing through *C*, and the image of the scale in *D* produced by total reflection appear in one and the same spot, so that the positions occupied by the spectrum lines may be read off on the scale. The prism is placed in about that position in which there is a minimum divergence of the rays of the sodium line; and the telescope is set in that direction in which the red and the violet potassium lines are about equidistant from the middle of the field of view.

The colorless flame into which the flame-coloring bodies are to be introduced, is placed 10 cm. from the slit. BUNSEN'S lamp, shown in fig. 22, gives the best flame. The lamp is adjusted so as to place the upper border of the chimney about 20 mm. below the lower end of the slit. When this lamp has been lighted, and a bead of substance—say of sulphate of potassa—introduced into the fusing zone by means of the holder shown in fig. 27, the iron disk of the spectrum apparatus, which, with all it carries, is moveable round its vertical axis, is turned until the point is reached where the luminosity of the spectrum is the most intense.

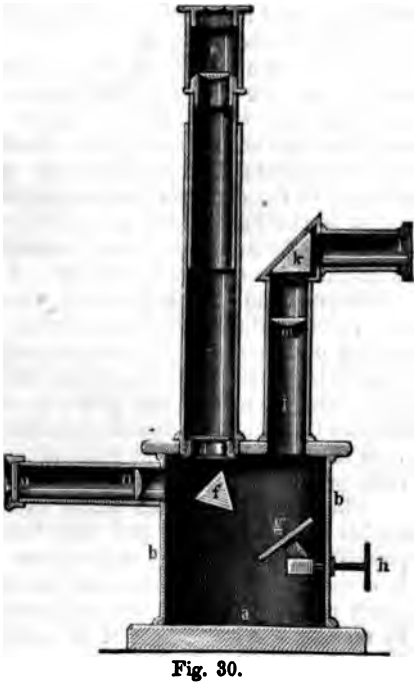

Fig. 30.

To cut off foreign light in all spectrum observations, the centre part of the apparatus is covered with a black cloth or card-board box.

REXROTH'S spectroscope, fig. 30, may be safely recommended as useful and economical.† It is very different in its arrangement from the apparatus just described. *b b* is a cylinder fixed onto the heavy disk *a*, and closely covered by *c*. *d e* is a telescope, and *i l* a bent tube,

* This arrangement is not very strong. For laboratories a more solid material such as brass would be much better than tin-foil.

† *Zeitschrift f.* anal. Chem., 3, 448.

which are fastened to *c*; *il* is so drawn that its internal construction may be plainly exhibited, *l* is a moveable slit, *k* is a reflecting prism, and *m* is a lens. The rays coming through the slit are made parallel by *m*, and then reflected from the mirror *g* onto the flint-glass prism *f*, by which they are refracted up the telescope. By means of the screw *i* it is possible to move *g* round a horizontal axis, and thus to bring the different points of the spectrum one after the other into the middle of the field of view. Opposite that side of *f* from which the rays leave the prism, is a side tube, *o*, containing the photographed scale and *n* being a lens by which the rays coming from *o* are made parallel; the rays are thus reflected from the upper face of the prism into the telescope, and become visible simultaneously with the spectrum. The scale is fixed, and being lighted by a small oil-lamp or a gas flame, is equally visible throughout the whole field of view. The sodium line is set by means of *k*, so that in the case of lines which are remote from each other, as for instance the blue potassium lines, we are enabled to read off their positions very conveniently on the scale, by moving the sodium line 20 divisions towards the left, and thus bringing the lines to be measured more into the middle of the field of view. Under these circumstances we should have to add 20 to the number read off, and on the other hand, if the sodium line were moved 20 divisions towards the right, in order to bring a red line more into the middle, 20 would have to be subtracted from the number read off.

The spectra produced by the alkalies, the alkaline earths, thallium and indium are shown in the picture at the commencement of the book. The solar spectrum has been added simply as a guide to the position and bearings of the lines. The spectra are represented as they appear in the apparatus furnished with an astronomic telescope. In the third section, in the chapters treating of the several bodies, attention will be called to the lines which are most characteristic for each metal. Here I will simply state the manner in which the highest degree of certainty is imparted to spectrum analysis. This is done by exposing the beads of the pure and unmixed metallic compounds to the flame, and marking on copied scales the position which the most striking spectrum lines occupy on the scale of the apparatus, in the manner shown, by way of illustration, in fig. 2 of the picture, with regard to the strontium spectrum. It is self-evident that the spectrum of an unknown substance can only pass for the strontium spectrum, if the characteristic lines not only agree with those of the latter in point of color, but appear also in exactly the same position where they are marked on the strontium scale.

The drawings of such scales every operator must, of course, make for his own apparatus; and they become useless for the intended purpose if any alteration is made in the position of the prism or the scale. It is therefore always advisable to set the apparatus so that it can be easily readjusted to its original position, which is most readily done by making the left border of the sodium line coincide with the number 50 of the scale.

With the introduction of spectrum analysis a new era has, in many respects, begun for chemical analysis, as by means of this discovery we can detect such minute quantities of bodies as by no other method. Spectrum analysis is marked moreover by a certainty above all doubt, *and gives results in* a few seconds, which could formerly be obtained *only, if at all, in hours* or days.

# APPENDIX TO SECTION I.

## § 18.

### APPARATUS.

As many students of chemical analysis might find some difficulty in the selection of the proper apparatus, I append here a list of the articles which are actually required for the performance of simple experiments and investigations, together with instructions to guide the student in the purchase or making of them.

1. A BERZELIUS SPIRIT LAMP (§ 16, fig. 14).

2. A GLASS SPIRIT LAMP (§ 16, fig. 16). Or, instead of these two, where coal-gas is procurable, a BUNSEN'S Gas-lamp, best one with chimney (§ 16, figs. 17, 18, and 22).

3. A BLOWPIPE (see § 15).

4. A PLATINUM CRUCIBLE. Select a crucible which will contain about a quarter of an ounce of water, with a cover shaped like a shallow dish; it must not be too deep in proportion to its breadth.

5. PLATINUM FOIL, as smooth and clean as possible, and not very thin: length about 40 mm.; width about 25 mm.

6. PLATINUM WIRE (see p. 18 and 24). Three stronger wires and three finer wires are amply sufficient. They are kept most conveniently in a glass filled with water, most of the beads being dissolved by that fluid when left in contact with it for some time; the wires may thus be kept always clean.

7. A STAND WITH TWELVE TEST TUBES—16 to 18 cm. is about the proper length of the tubes, from 1 to 2 cm. the proper width. The tubes must be made of thin white glass, and so well annealed that they do not crack even though boiling water be poured into them. The rim must be quite round, and slightly turned over; it ought not to have a lip, as this is useless and simply prevents the tube being closely stopped with the finger, and also shaking the contents. The stand shown in fig. 31 will be found most suitable. The pegs on the upper shelf serve for the clean tubes, which may thus be well drained.

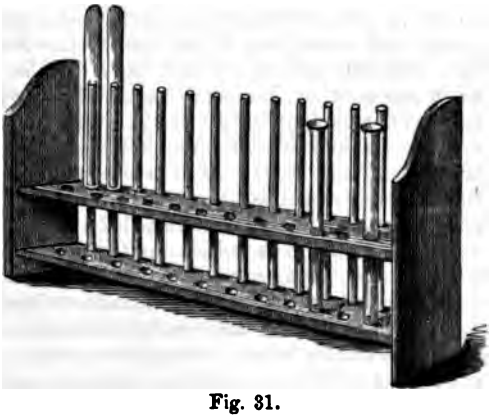

Fig. 31.

8. SEVERAL BEAKERS AND SMALL FLASKS of thin, well annealed glass.

9. SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN *CRUCIBLES*. Those of the royal manufacture of *Berlin are unexceptionable, both* in shape and durability. Meissen *and Nymphenburg porcelain will also* answer the purpose.

10. SEVERAL GLASS FUNNELS of various sizes. They must be inclined at an angle of 60°, and merge into the neck at a definite angle.

11. A WASHING BOTTLE of a capacity of from 300 to 400 c.c. (see § 7).

12. SEVERAL GLASS RODS AND GLASS TUBES. The latter are bent, drawn out, &c., over a Berzelius lamp or gas-lamp; the former are rounded at the ends by fusion.

13. A selection of WATCH-GLASSES.

14. A small AGATE MORTAR.

15. A pair of small STEEL or BRASS PINCERS, about four or five inches long.

16. A WOODEN FILTER STAND (see § 5).

17. A TRIPOD of thin iron, to support the dishes, &c., which it is intended to heat over the small spirit or gas lamp.

18. The Colored Glasses described in § 17, especially blue and green.

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# SECTION II.

## REAGENTS.

### § 19.

A VARIETY of phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, &c. Now if these phenomena are very striking, and attend only upon the action of two definite bodies upon one another, it is obvious that the presence of one of these bodies may be detected by means of the other: if we know, for instance, that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that, if upon adding baryta to any liquid, we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called *reagents*.

According to the different objects attained by the application of these bodies, we make a distinction between *general* and *special* reagents. By general reagents we understand those which serve to determine the class or group to which a substance belongs; and by special reagents those which serve to detect bodies individually. That the line between the two divisions cannot be drawn with any degree of precision, and that one and the same substance is often made to serve both as a general and a special reagent, cannot well be held a valid objection to this classification, which is in fact simply intended to induce a habit of employing reagents always for a settled purpose—viz., either simply to find out the group to which the substance belongs, or to determine the latter individually.

Now whilst the usefulness of general reagents depends principally upon their efficiency in strictly characterizing groups of bodies, and often

effecting a complete separation of the bodies belonging to one group from those belonging to another, that of special reagents depends upon their being characteristic and sensitive. We call a reagent *characteristic*, if the alteration produced by it, in the event of the body tested for being present, is so distinctly marked as to admit of no mistake. Thus iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena produced by these reagents—viz., the separation of metallic copper and of globules of mercury—admit of no mistake. We call a reagent *sensitive* or *delicate*, if its action is distinctly perceptible, even though a very minute quantity only of the substance tested for be present; such is, for instance, the action of starch upon iodine.

Very many reagents are both characteristic and delicate; thus, for instance, terchloride of gold for protoxide of tin; ferrocyanide of potassium for sesquioxide of iron and oxide of copper, &c.

I need hardly mention that, as a general rule, reagents must be chemically pure—*i.e.*, they must consist purely and simply of their essential constituents, and must contain no admixture of foreign substances. We must therefore make it an invariable rule to test the purity of our reagents before we use them, no matter whether they be articles of our own production or purchased. Although the necessity of this is fully admitted on all hands, yet we find that in practice it is too often neglected; thus it is by no means uncommon to see alumina entered among the substances detected in an analysis, simply because the solution of potassa used as one of the reagents happened to contain that earth; or iron, because the chloride of ammonium used was not free from that metal. The directions given in this section for testing the purity of the several reagents refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "addition in excess," "supersaturation," &c., often induce novices to suppose that they cannot add too much of the reagent, and thus some will fill a test tube with acid, simply to supersaturate a few drops of an alkaline fluid, whereas every drop of acid added, after the neutralization point has once been reached, is to be looked upon as an excess of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent added in insufficient quantity often produces phenomena quite different from those which will appear if the same reagent be added in excess: *e.g.*, a solution of chloride of mercury yields a white precipitate if tested with a small quantity of hydrosulphuric acid; but if treated with the same reagent in excess, the precipitate is black. Experience has, however, proved that the most common mistake beginners make, is to add the reagents too copiously. One reason why this over-addition must impair the accuracy of the results is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that therefore they may be the more readily overlooked the nearer we approach these limits by diluting the fluid. Another reason is in the fact that a large excess of a reagent will often have a solvent or modifying action upon a precipitate or color, and will entirely prevent the exhibition of phenomena which a suitable quantity would without difficulty produce.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down, which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: let the student always reflect before the addition of a reagent for what purpose he applies it, what are the phenomena he intends to produce, and what are the results of the addition of excess.

We divide reagents into two classes, according to whether the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is brought about by the application of heat, or by means of liquid solvents; we have consequently, 1, *Reagents in the wet way;* and 2, *Reagents in the dry way.* For greater clearness we subdivide these two principal classes as follows:—

A. REAGENTS IN THE WET WAY.

I. SIMPLE SOLVENTS.

II. ACIDS and HALOGENS.

*a.* Oxygen acids.
*b.* Hydrogen acids and halogens.
*c.* Sulphur acids.

III. BASES and METALS.

*a.* Oxygen bases.
*b.* Sulphur bases.

IV. SALTS.

*a.* Of the alkalies.
*b.* Of the alkaline earths.
*c.* Of the oxides of the heavy metals.

V. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOWPIPE REAGENTS.

## A. REAGENTS IN THE WET WAY.

### I. SIMPLE SOLVENTS.

Simple solvents are fluids which do not enter into chemical combination with the bodies dissolved in them; they will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is in a measure dependent upon the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, color, &c.) are not destroyed by the solvent. (See § 2.)

## § 20.

### 1. Water (HO).

*Preparation.*—Pure water is obtained by distilling spring water om a copper still with head and condenser made of pure tin, or from glass retort; which latter apparatus, however, is less suitable for the urpose. The distillation is carried to about three-fourths of the uantity operated upon. If it is desired to have the distilled water erfectly free from carbonic acid and carbonate of ammonia, the porions passing over first must be thrown away. In the larger chemical nd in most pharmaceutical laboratories, the distilled water required is btained from the steam apparatus which serves for drying, heating, oiling, &c. Rain water collected in the open air may in many cases e substituted for distilled water.*

*Tests.*—It must be colorless, odorless and tasteless, and should not eave the smallest residue when evaporated in a platinum vessel. It hould not be changed by sulphide of ammonium (copper, lead, iron), nor endered turbid by baryta water (carbonic acid). No cloudiness should e caused even after long standing by the addition of oxalate of mmonia (lime), of chloride of barium and hydrochloric acid (sulphuric cid), of nitrate of silver and nitric acid (chlorides), or of chloride of ercury and carbonate of soda (ammonia).

*Uses.*—We use water† principally as a simple solvent for a great ariety of substances; the most convenient way of using it is with the ashing bottle (see § 7, fig. 3), by which means a stronger or finer tream may be obtained. It serves also to effect the conversion of everal neutral metallic salts (more particularly terchloride of antimony nd the salts of bismuth) into soluble acid and insoluble basic compounds.

## § 21.

### 2. Alcohol ($C_4H_6O_2$).

*Preparation.*—Two sorts of alcohol are used in chemical analyses: viz., lst, spirit of wine of ·83 or ·84 sp. gr. = 91 to 88 per cent. by volume *spiritus rectificatus* of the British Pharmacopœia); and 2nd, absolute lcohol. The latter may be prepared most conveniently by mixing, in distilling vessel, 1 part of fused chloride of calcium with 2 parts of ectified spirit of wine of about 90 per cent. by volume, digesting the ixture 2 or 3 days, until the chloride of calcium is dissolved, and hen distilling slowly and in fractional portions. So long as the distilate shows a specific gravity below ·810 (= 96·5 per cent. by volume), t may pass for absolute alcohol. The portions coming over after are eceived in a separate vessel.

*Tests.*—Pure alcohol must completely volatilize, and ought not to eave the least smell of fusel oil when rubbed between the hands; or should it alter the color of moist blue or red litmus paper. When indled, it must burn with a faint bluish barely perceptible flame.

* As regards the preparation *of water* absolutely free from organic matter, see RAS, *Zeitschrift f. anal. Chem. 6, 417.*

† *In analytical experiments we use only* distilled water; whenever, therefore, the *m water occurs in the present work,* distilled water is meant.

*Uses.*—Alcohol serves, (*a*) to effect the separation of bodies soluble in this fluid from others which do not dissolve in it, *e.g.* of chloride of strontium from chloride of barium; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, *e.g.* gypsum, malate of lime; (*c*) to produce various kinds of ether, *e.g.* acetic ether, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, mostly with the co-operation of an acid, certain peroxides and metallic acids, *e.g.* binoxide of lead, chromic acid, &c.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boracic acid, strontia, potassa, soda, and lithia.

## § 22.

### 3. Ether ($C_4H_5O$).

### 4. Chloroform ($C_2HCl_3$).

### 5. Sulphide of Carbon ($CS_2$).

These solvents find but limited application in the qualitative analysis of inorganic bodies. They serve indeed almost exclusively to detect and isolate bromine and iodine. Chloroform and sulphide of carbon are preferable to ether in this respect. The latter is used for the detection of chromic acid by means of peroxide of hydrogen. These preparations are made much better on a large than on a small scale, and the best way therefore is to procure them by purchase.

*Tests.*—*Ether* must have a specific gravity of ·713 at 20°, and require 9 parts of water for solution. The solution must not alter the color of test papers. Ether must, even at the common temperature, rapidly and completely evaporate on a watch-glass. *Chloroform* must be colorless and transparent and have a specific gravity of 1·48. It must have no acid reaction, nor impair the transparency of solution of nitrate of silver. Mixed with 2 vols. of water, and shaken, its volume must not appear perceptibly diminished. It must even at the common temperature readily and completely evaporate on a watch-glass. *Sulphide of carbon* should be colorless, readily and completely volatile even at the common temperature, and exercise no action upon carbonate of lead.

## II. Acids and Halogens.

## § 23.

The acids—at least those of more strongly pronounced character—are soluble in water. The solutions taste acid and redden litmus paper. Acids are divided into oxygen acids, sulphur acids, and hydrogen acids.

The *oxygen acids*, produced generally by the combination of a non-metallic element with oxygen, combine with water in definite proportions to hydrated acids. It is with these hydrates that we have usually to do in analytical processes; they are contained in the aqueous solutions of the acids, and are commonly designated by the simple name of the free acid, as the accession of water does not destroy their acid properties. In the action of hydrated acids upon oxides of metals, the oxide takes *the place of the* water of hydration, and an oxygen salt is formed ($HO, SO_3 + KO = KO, SO_3 + HO$). Where these salts are the pr

duct of the combination of an acid with a strong base, their reaction (supposing the combining acid also to be a strong acid) is neutral; the salts formed with weaker bases, for instance with the oxide of a heavy metal, generally show acid reaction, but are nevertheless called neutral salts if the oxygen of the base bears the same proportion to that of the acid in which it is found in the distinctly neutral salts of the same acid, or, in other terms, if it corresponds with the saturation capacity of the acid. Sulphate of potassa ($KO, SO_3$) has a neutral reaction, whilst the reaction of sulphate of copper ($CuO, SO_3$ + 5aq.) is acid; yet the latter is nevertheless called neutral sulphate of copper, because the oxygen of the oxide of copper in it bears a proportion of 1 : 3 to that of the sulphuric acid, which is the same proportion as the oxygen of the potassa bears to that of the sulphuric acid in the confessedly neutral sulphate of potassa.

The *hydrogen acids* are formed by the combination of the halogens with hydrogen. Most of these possess the characteristic properties of acids in a high degree. They neutralize oxygen bases, with formation of haloid salts and water; HCl and NaO = NaCl and HO,—3 HCl and $Fe_2O_3$ = $Fe_2Cl_3$ and 3 HO. The haloid salts produced by the action of powerful hydrogen acids upon strong bases have a neutral reaction; whilst the solutions of those haloid salts that have been produced by the action of powerful hydrogen acids upon weak bases (such as alumina and sesquioxide of iron) have an acid reaction.

The *sulphur acids* are more frequently the result of the combination of metallic than of non-metallic elements with sulphur; they combine with sulphur bases to sulphur salts; HS + KS = KS, HS—$AsS_3$ + 3 NaS = 3 NaS, $AsS_3$. The sulphur acids being weak acids, the soluble sulphur salts have all of them alkaline reaction.

### *a.* Oxygen Acids.

### § 24.

### 1. Sulphuric Acid ($HC, SO_3$).

We use—

*a. Concentrated sulphuric acid of commerce.*

*b. Concentrated pure sulphuric acid.*

The following methods may be recommended for preparing chemically pure sulphuric acid:

*a.* Put 1000 grm. of ordinary concentrated sulphuric acid in a porcelain dish, add 3 grm. of sulphate of ammonia, and heat till copious fumes of sulphuric acid begin to escape. This is done in order to destroy the oxides of nitrogen which are generally present in minute quantity. After cooling, add 4 or 5 grm. of coarsely-powdered binoxide of manganese, and heat to boiling with stirring, in order to convert any arsenious acid into arsenic acid (Blondlot). When cool pour off the clear fluid by means of a long funnel tube into a coated retort. The retort should not be more than half full, and is to be heated directly over charcoal. To prevent bumping, it is advisable to rest the retort on an inverted crucible cover, so that the sides may be more heated than the bottom. The neck of the retort must reach so far into the receiver that the acid distilling over drops directly into the body. To cool the receiver by means of water is unnecessary and even dangerous. To

prevent the receiver coming into actual contact with the hot neck of the retort, some asbestos in large fibres is placed between them. When about 10 or 15grm. has been drawn over, change the receiver and distil off three-fourths of the contents of the retort. This method depends on the fact discovered by BUSSY and BUIGNET, that on distilling sulphuric acid which contains arsenic in the form of arsenic acid an arsenic-free distillate is obtained.

*β.* Pour into 4 parts of water 1 part of concentrated sulphuric acid, and conduct into the mixture for some time a slow stream of hydrosulphuric acid, keeping the fluid heated to 70°. Let the mixture stand at rest for several days, then decant the clear supernatant fluid from the precipitate, which consists of sulphur, sulphide of lead, perhaps also sulphide of arsenic, and heat the decanted fluid in a tubulated retort with obliquely upturned neck and open tubulature until sulphuric acid fumes escape with the aqueous vapor. The acid so purified is fit for many purposes of chemical analysis; if it is wished, however, to free it also from non-volatile substances, it may be distilled from a coated retort as in *α*. As soon as the drops in the neck of the retort become oily, the receiver is changed, and the concentrated acid which now passes over is kept in a separate vessel.

*c. Common dilute sulphuric acid.* This is prepared by adding to 5 parts of water in a leaden or porcelain dish gradually, and whilst stirring, 1 part of concentrated sulphuric acid. The sulphate of lead which separates is allowed to subside, and the clear fluid finally decanted.

*Tests.*—Pure sulphuric acid must be colorless; when colorless solution of sulphate of protoxide of iron is poured upon it in a test tube, no brown tint must mark the plane of contact of the two fluids (nitric acid, hyponitric acid); when diluted with twenty parts of water it must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (hyponitric acid). Mixed with pure zinc and water, it must yield hydrogen gas, which, on being passed through a red-hot tube, must not deposit the slightest trace of arsenic. It must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with four or five parts of spirit of wine (oxide of lead, sesquioxide of iron, lime). The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test tube. If the plane of contact is marked by turbidity (chloride of lead), lead is present. Sulphurous acid is discovered by the odor after shaking the acid in a half-filled bottle.

*Uses.*—Sulphuric acid has for most bases a greater affinity than almost any other acid; it is therefore used principally for the liberation and expulsion of other acids, especially phosphoric, boracic, hydrochloric, nitric, and acetic acids. Several substances which cannot exist in an anhydrous state (*e.g.* oxalic acid), are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is owing to the great affinity which sulphuric acid possesses for water. The nature of the decomposed body may in such cases be inferred from the liberated products of decomposition. Sulphuric acid is also frequently used for the evolution of certain gases, more particularly of hydrogen and hydrosulphuric acid. It serves also as a special reagent for the detection and precipitation of baryta, strontia, and lead. What kind of sulphuric acid *is to be used, whether the* pure acid or the ordinary acid of commerce, *whether concentrated or dilute,* depends upon what the circumstances

in each case may require. It will, however, be found that the necessary directions on this point are generally given in the present work.

## § 25.

### 2. Nitric Acid ($HO, NO_5$).

*Preparation.*—*a.* Heat crude nitric acid of commerce, as free as possible from chlorine, and of a specific gravity of at least 1·31,* in a glass retort to boiling, with addition of some nitrate of potassa; let the distillate run into a receiver kept cool, and try from time to time whether it still continues to precipitate or cloud solution of nitrate of silver. As soon as this ceases to be the case, change the receiver, and distil until a trifling quantity only remains in the retort. Dilute the distillate with water until the specific gravity is 1·2.

*b.* Dilute crude nitric acid of commerce of about 1·38 specific gravity with two-fifths of its weight of water, and add solution of nitrate of silver as long as a precipitate of chloride of silver continues to form; then add a further slight excess of solution of nitrate of silver, let the precipitate subside, decant the perfectly clear supernatant acid into a retort or an alembic with ground head; add some nitrate of potassa free from chlorine, and distil until only a small quantity remains, taking care to attend to the proper cooling of the fumes distilling over. Dilute the distillate, if necessary, with water until it has a specific gravity of 1·2.

*Tests.*—Pure nitric acid must be colorless and leave no residue upon evaporation on platinum foil. Addition of solution of nitrate of silver or of nitrate of baryta must not cause the slightest turbidity in it. It is advisable to dilute the acid with water before adding these reagents, as otherwise nitrates will precipitate. Silver should be tested for by hydrochloric acid.

*Uses.*—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, &c. With metals and sulphides of metals the acid first oxidizes the metal present, at the expense of part of its own oxygen, and then dissolves the oxide to a nitrate. Most oxides are dissolved by nitric acid at once as nitrates; and so are also most of the insoluble salts with weaker acids, the latter being expelled in the process by the nitric acid. Nitric acid dissolves also salts with soluble non-volatile acids, as *e.g.* phosphate of lime, with which it forms nitrate of lime and acid phosphate of lime. Nitric acid is used also as an oxidizing agent: for instance, to convert protoxide of iron into sesquioxide, protoxide of tin into binoxide, &c.

## § 26.

### 3. Acetic Acid ($HO, C_4H_3O_3 = HO, \bar{A}$).

A highly concentrated acetic acid is not required in qualitative analytical processes; the *acidum aceticum* of the British Pharmacopœia, which contains 33 per cent. of HO, $C_4H_3O_3$, and has a specific gravity of 1·044, fully answers the purpose.

*Tests.*—Pure acetic acid must leave no residue upon evaporation, and —after saturation with carbonate of soda—emit no empyreumatic odor. Hydrosulphuric acid, solution of nitrate of silver, and solution of nitrate

* *A weaker acid will not answer the purpose.*

of baryta must not color or cloud the dilute acid, nor must sulphide of ammonium after neutralization of the acid by ammonia. Solution of indigo must not lose its color when heated with the acid. Empyreumatic matter is best detected by neutralizing the acid with carbonate of soda, and adding permanganate of potash solution. If the solution loses its color and afterwards deposits a brown precipitate, empyreumatic matter is present.

If the acid is not pure, add some acetate of soda and redistil from a glass retort not quite to dryness; if it contains sulphurous acid (in which case hydrosulphuric acid will produce a white turbidity in it), digest it first with some binoxide of lead or finely-pulverized binoxide of manganese, and then distil with acetate of soda.

*Uses.*—Acetic acid possesses a greater solvent power for some substances than for others; it is used therefore to distinguish the former from the latter; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. Acetic acid is occasionally used also to acidulate fluids where it is wished to avoid the employment of mineral acids.

§ 27.

### 4. Tartaric Acid ($2\,HO, C_8H_4O_{10} = 2\,HO, \bar{T}$).

The tartaric acid of commerce is sufficiently pure for the purposes of chemical analysis. It is kept best in powder, as its solution suffers decomposition after a time. For use it is dissolved in a little water with the aid of heat.

*Uses.*—The addition of tartaric acid to solutions of sesquioxide of iron, alumina, and various other oxides of metals, prevents the usual precipitation of these metals by an alkali; this non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may therefore be employed to effect the separation of these metals from others the precipitation of which it does not prevent. Tartaric acid forms a difficultly soluble salt with potassa, but not so with soda; it is therefore one of our best reagents to distinguish between the two alkalies. *Bitartrate of soda* answers this latter purpose still better than the free acid. This reagent is prepared by dissolving one of two equal portions of tartaric acid in water, neutralizing the solution with carbonate of soda, then adding the other portion of the acid, and evaporating the solution to the crystallization point. For use, 1 part of the salt is dissolved in 10 parts of water.

## *b.* Hydrogen Acids and Halogens.

§ 28.

### 1. Hydrochloric Acid (HCl).

*Preparation.*—Pour a cooled mixture of seven parts of concentrated sulphuric acid and two parts of water over four parts of chloride of sodium in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath until the evolution of gas ceases; conduct the evolved gas, by *means of a bent tube, into* a flask containing six parts of water, and take *care to keep this vessel* constantly cool. To prevent the gas from

receding the tube ought only to dip about one line into the water of the flask. When the operation is terminated, try the specific gravity of the acid produced, and dilute with water until it marks from 1·11 to 1·12. If you wish to ensure the absolute purity of the acid, and its perfect freedom from every trace of arsenic and chlorine, you must take care to free the sulphuric acid intended to be used in the process from arsenic and the oxygen compounds of nitrogen, according to the directions of § 24. A pure acid may also be prepared cheaply from the crude hydrochloric acid of commerce by diluting the latter to a specific gravity of 1·12, and distilling the fluid, with addition of some chloride of sodium. Or you may put the acid into the retort in the concentrated form, placing 60 parts of water into the receiver for every 100 parts of concentrated acid, and not luting the receiver to the retort. If the crude acid contains chlorine this should be removed first by cautious addition of solution of sulphurous acid, before proceeding to the distillation; if, on the other hand, it contains sulphurous acid, this is removed in the same way by cautious addition of some chlorine water. Hydrochloric acid not unfrequently contains chloride of arsenic, owing to the presence of arsenic in the sulphuric acid employed. To free it from this impurity, the acid is mixed with twice its volume of water, hydrosulphuric acid is conducted into it, the mixture allowed to stand at rest for some time, the clear fluid then decanted from the sulphur and sulphide of arsenic, and heated, to expel the sulphuretted hydrogen.

*Tests.*—Hydrochloric acid must be perfectly colorless and leave no residue upon evaporation. If it turns yellow on evaporation, sesquichloride of iron is present. It must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (chlorine or sesquichloride of iron), nor discolor a fluid made faintly blue with iodide of starch (sulphurous acid). Chloride of barium ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Hydrosulphuric acid must leave the diluted acid unaltered (arsenic). After neutralization with ammonia, sulphide of ammonium must produce no change in it (iron, thallium).

*Uses.*—Hydrochloric acid serves as a solvent for a great many substances. It dissolves many metals and sulphides of metals as chlorides, with evolution of hydrogen or of hydrosulphuric acid. It dissolves oxides and superoxides in the form of chlorides, in the latter case mostly with liberation of chlorine. Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts with non-volatile and soluble acids apparently without decomposing them (*e.g.* phosphate of lime); but the fact is that in cases of this kind a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed; thus, for instance, in the case of phosphate of lime, chloride of calcium and acid phosphate of lime are formed. With salts of acids forming no soluble acid compound with the base present hydrochloric acid forms metallic chlorides, the liberated acids remaining free in solution (borate of lime). Hydrochloric acid is also applied as a special reagent for the detection and separation of oxide of silver, suboxide *of mercury, and lead,* and likewise for the detection of *free ammonia, with which it produces* in the air dense white fumes of *chloride of ammonium.*

## § 29.

### 2. Chlorine (Cl) and Chlorine Water.

*Preparation.*—Mix 18 parts of common salt in lumps with 15 parts of *finely pulverized* good binoxide of manganese, free from carbonate of lime; put the mixture in a flask, pour a *completely cooled* mixture of 45 parts of concentrated sulphuric acid and 21 parts of water upon it, and shake the flask: a uniform and continuous evolution of chlorine gas will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. This method of Wiggers is excellent, and can be highly recommended. Conduct the chlorine gas evolved first through a flask containing a little water, then into a bottle filled with cold water, and continue the process until the fluid is saturated. Where it is desired to obtain chlorine water quite free from bromine, the washing flask is changed after about one-half of the chlorine has been expelled, and the gas which now passes over is conducted into a fresh bottle filled with water. If the chlorine water is to be quite free from hydrochloric acid, the gas must be passed through a U tube containing binoxide of manganese. The chlorine water must be kept in a cellar and carefully protected from the action of light; since, if this precaution is neglected, it speedily suffers complete decomposition, being converted into dilute hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle protected from the influence of light by a case of pasteboard. Chlorine water which has lost its strong peculiar odor is unfit for use.

*Uses.*—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Chlorine serves moreover to effect the solution of certain metals (gold, platinum), to decompose metallic sulphides, to convert sulphurous acid into sulphuric acid, protoxide of iron into sesquioxide, &c.; and also to effect the destruction of organic substances, as in presence of these it withdraws hydrogen from the water, enabling thus the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For this latter purpose it is most advisable to evolve the chlorine in the fluid which contains the organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture, and then adding chlorate of potassa. This gives rise to the formation of chloride of potassium, water, free chlorine, and bichlorate of chlorous acid, which acts in a similar manner to chlorine.

## § 30.

### 3. Nitro-Hydrochloric Acid. *Aqua regia.*

*Preparation.*—Mix 1 part of pure nitric acid with from 3 to 4 parts of pure hydrochloric acid.

*Uses.*—Nitric acid and hydrochloric acid decompose each other, the decomposition mostly resulting, as Gay-Lussac has shown, in the formation of two compounds which are gaseous at the ordinary temperature, $NO_2Cl$ and $NO_2Cl$, and of free chlorine and water. Thus, $HO, NO_5$

$+3\,H\,Cl = N\,O_2\,Cl_2 + Cl + 4\,H\,O$ and $H\,O,\,N\,O_2 + 3\,H\,Cl = N\,O_2\,Cl + 2\,Cl + 4\,H\,O$. This decomposition ceases as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the acids named, makes aqua regia our most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which metals are insoluble both in hydrochloric and in nitric acid; and also to decompose various metallic sulphides, *e.g.* cinnabar, pyrites, &c.

## § 31.

### 4. Hydrofluosilicic Acid ($Si\,F_2$, $H\,F$).

*Preparation.*—Take 1½ part of powdered glass, or 1 part of powdered ignited flint, or 1 part of quartz sand. Whichever is used, it must have been washed from every particle of dust, and then ignited. Mix intimately with one part of perfectly dry fluor spar in powder; pour nine parts of concentrated sulphuric acid over the mixture in a non-tubulated retort, which it is advisable to coat with clay, and mix carefully by shaking the vessel. As the mixture swells up when getting warm, it must at first fill the retort only to one-third. The neck of the retort is connected air-tight with a small tubulated receiver, and the tubulus of the latter again, by means of indiarubber, with a wide glass tube twice bent at a right angle. To the descending limb of the glass tube a funnel is attached by means of indiarubber; this funnel is lowered into a beaker containing four parts of water. Promote the disengagement of fluosilicic gas, which commences even in the cold, by moderately heating the retort over charcoal. Towards the end of the process a pretty strong heat should be applied. Every gas bubble produces in the water a precipitate of hydrated silicic acid, with simultaneous formation of hydrofluosilicic acid, $3\,Si\,F_2 + 2\,H\,O = 2\,(Si\,F_2,\,H\,F) + Si\,O_2$. The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the descending limb of the tube cannot be allowed to dip direct into the water, since it would in that case speedily be choked. It sometimes happens in the course, and especially towards the end of the operation, that complete channels of silica are formed in the gelatinous liquid, through which the gas gains the surface without undergoing decomposition if the liquid is not occasionally stirred. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth, squeeze the fluid through, and filter it afterwards. Keep the filtrate for use.

*Tests.*—Hydrofluosilicic acid must produce no precipitate in solutions of salts of strontia (sulphate of strontia).

*Uses.*—Bases decompose with hydrofluosilicic acid, forming water and metallic silicofluorides. Many of these are insoluble, whilst others are soluble; the latter may therefore by means of this reagent be distinguished from the former. In the course of analysis hydrofluosilicic acid is applied *simply for the detection* and separation of baryta.

## c. Sulphur Acids.

### § 32.

### 1. Hydrosulphuric Acid. *Sulphuretted Hydrogen* (H S).

*Preparation.*—Hydrosulphuric acid gas is evolved best from sulphide of iron, which is broken into small lumps and then treated with dilute sulphuric or hydrochloric acid. Fused sulphide of iron may be procured so cheaply in commerce that it is hardly worth while to take the trouble of preparing it. However, if you wish to prepare it yourself, this may be done by heating iron turnings, or 1 to 1½ inch iron nails, in a covered Hessian crucible to a white heat, and then adding small lumps of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this is the case, pour the fused mass onto sand, or into an old Hessian crucible. Or make a hole in the bottom of the crucible in which you fuse the mass, when the sulphide of iron will as fast as it forms run through the hole in the bottom of the crucible, and may thus be easily received in a coal-shovel placed in the ash-pit. Or introduce an intimate mixture of thirty parts of iron filings and twenty-one parts of flowers of sulphur in small portions into a red-hot crucible, awaiting always the incandescence of the portion last introduced before proceeding to the addition of a fresh one. When you have thus put the whole mixture into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to make the sulphide of iron fuse more or less.

Fig. 32.

The evolution of the gas is effected in the apparatus illustrated by fig. 32. Pour water over the sulphide of iron in *a*, add concentrated sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, pour the fluid off the still undecomposed sulphide of iron, rinse the bottle repeatedly with water, then fill it with that fluid, and keep it for the next operation. If you neglect this, the apparatus will speedily become incrusted with crystals of sulphate of protoxide of iron, which is apt to interfere injuriously with subsequent processes of evolution of gas.

For larger laboratories, or for chemists having to operate often and largely with hydrosulphuric acid, a gasometer may be used, or the following apparatus, devised by Brugnatelli, and modified as shown in fig. 33. The flask, B, is provided with a tubulure at *a*;* its neck is filled with broken glass, its body with sulphide of iron in small pieces. The indiarubber stopper in the neck contains two tubes—*s* (which may

* Flasks with a lateral tubulure, such as are generally used for receivers, are also *applicable, and indeed one of these will be found in the original drawing (Zeitschrift f. anal. Chem. 6, 390).* But it is certainly better to have the tubulure at the top.

sometimes be omitted, see below), and the short tube *c*, which must have *a bore of* 1 cm. *at least;* the latter is connected with the tube *d* of the same size by means of indiarubber. The tube *e* extends almost to the bottom of A, and is connected on the other side with the bottle M by means of the indiarubber tube *f*. M is closed with a cork or indiarubber stopper, containing a small tube open at both ends. The stopper in the tubulure *a* of the flask B contains a glass tube, which is in con-

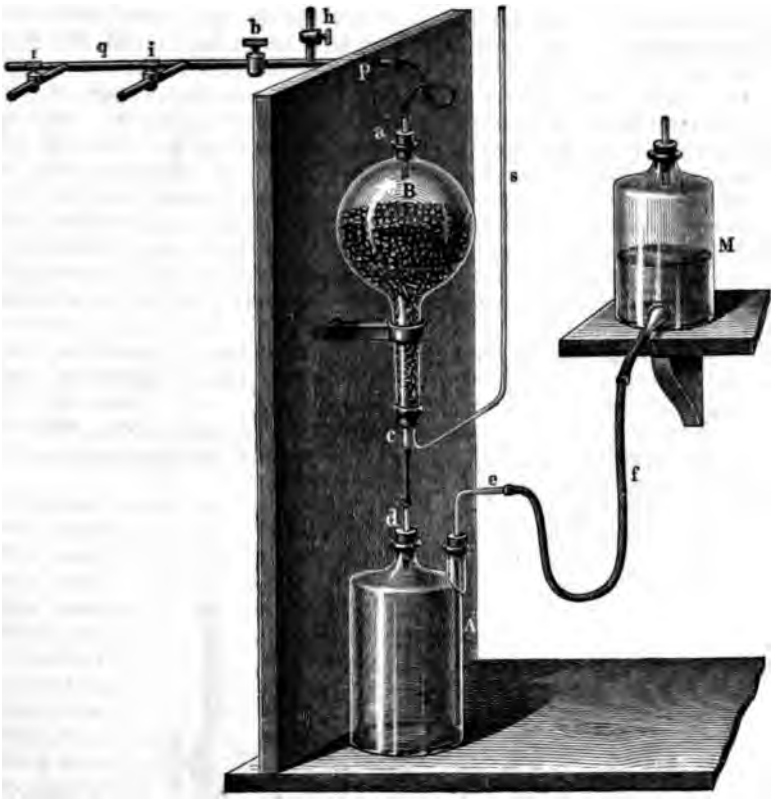


Fig. 33.

nexion with a leaden pipe. The latter conducts the gas, and is supplied with the brass cocks *h*, *b*, *i i*.

To set the apparatus going, open *h*, and fill M with a mixture of 1 volume common hydrochloric acid and 2 volumes water. The fluid will pass into A, fill the bottle, and rise through *d* and *c* into the flask B. As soon as the neck of the latter is nearly full, close the cock *h*, and take care that M is not more than half full. If now *b* is opened, and also *i*, the acid rises up to the sulphide, the evolution of gas commences and proceeds *with great regularity*, since the wide tubes c and d allow *the constant descent of the solution* of protochloride of iron and ascent *of fresh acid. If the acid* does not rise in B as high as is wished, place

one or two blocks of wood under M. The current of gas may be entirely regulated by raising or lowering M, as BRUGNATELLI recommends, but the cocks will be found necessary in large laboratories where the gas has to be passed into several different fluids at the same time. If the apparatus is not required for some time, M should be placed lower; the fluid will thus sink in B, and ceasing to be in contact with the sulphide of iron, the evolution of gas will cease. In this case, if the evolution of gas in B is not rapid enough to fill the space vacated by the fluid, air will enter through the tube *s*. If the tube *s* is present at all, it should be sufficiently long to prevent the exit of fluid when there is a pressure of gas. After the acid has flowed from B, the still moist sulphide of iron may continue evolving gas, but this will merely occasion more acid to pass from A to M. The tube *s* may be left out when the cocks are used. Under these circumstances the fluid in B will descend more slowly on lowering M, since the space filled by the descending acid has to be occupied by sulphuretted hydrogen. When there are no cocks, however, *s* is essential; otherwise on lowering M, the fluid through which the gas is passing might recede into the apparatus. This inconvenience may be easily prevented where cocks are provided, simply by closing *b* before lowering M. The gas from *i i* is conducted through wash-bottles, or in winter through U tubes filled with wool before being used.

When the acid is finally exhausted, M is placed lower than A, and the air-cock *h* is opened, if the tube *s* is not present. All the fluid then passes into M, and can be poured away.

I am so pleased with the working of this apparatus that I now use it instead of the large leaden generator which has rendered me such good service for so many years.

Fig. 34.

ollowing apparatus (fig. 34), devised by Fr. Mohr, depends upon principle as the above; it is particularly useful for the evolution quantities of the gas. A is a well-known piece of apparatus, lrying large quantities of gas with chloride of calcium; at *b* is a d disk of lead, and above lumps of sulphide of iron. To the is fixed, by means of indiarubber *a*, a small piece of wide glass ich is filled with cotton wool, and is intended to stop any par- protochloride of iron which may be spirted up. *c* is a glass h a long wooden handle, which may be replaced by a clip; *e* a solution of carbonate of soda, to prevent the escape of the tted hydrogen from the solution of protochloride of iron, and to he latter from the action of the air. The acid used here is a of common hydrochloric acid with one or two measures of water. e are many other forms of apparatus used for the same purpose. ised by Pohl is simple and convenient to use. It is shown in

The bottle A, which contains dilute : acid, should hold from 2 to 2½ litres. l glass rod G, measuring at least 9 mm. ter, and with the upper end ground, y tightly into the indiarubber stopper it it requires a certain degree of force it upwards or downwards. To the d of this rod is attached the perforated , made of vulcanite. This basket is th coarse linen, and filled with lumps ide of iron. If the glass rod G is down sufficiently far just to dip into te sulphuric acid in A, a slow stream sulphuric acid is evolved, which may ased by lowering the basket, or stopped ring it up out of reach of the fluid 'he wide tube R is filled with cotton id serves the purpose of a washing-

Fig. 35.

*uretted hydrogen water (solution of hydro- acid*) is prepared by conducting the very cold water, which has been pre- reed from air by boiling. The opera- continued until the water is completely saturated with the gas, ay be readily ascertained by closing the mouth of the flask thumb, and shaking it a little: if upon this a pressure is felt hin, the operation may be considered at an end; but if, on the , the thumb feels sucked into the mouth of the flask, this is a n that the water is still capable of absorbing more gas. Sul- d hydrogen water must be kept in well-closed vessels, other- will soon suffer complete decomposition, the hydrogen being to water, and a small portion of the sulphur to sulphuric rest of the sulphur separating. The best way of preserving it d for a very long time is to pour the freshly prepared solution tely into small phials, to cork these well, and to place them in ted position in *small jars filled* with water. Pure sulphuretted *n water must be perfectly* clear and strongly emit the peculiar *ie gas; when treated with* sesquichloride of iron, it must yield

a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it. It must leave no residue upon evaporation on platinum.

*Uses.*—Hydrosulphuric acid has a strong tendency to undergo decomposition with metallic oxides, forming water and metallic sulphides, which latter being mostly insoluble in water are usually precipitated in the process. The conditions under which the precipitation of certain sulphides ensues differ materially; by altering or modifying these conditions we may therefore divide the whole of the precipitable metals into groups, as will be found explained in Section III. Hydrosulphuric acid is therefore an invaluable agent to effect the separation of metals into groups. Some of the precipitated sulphides exhibit a characteristic color indicative of the individual metals which they respectively contain. The great facility with which hydrosulphuric acid is decomposed renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce salts of sesquioxide of iron to salts of protoxide, chromic acid to the state of sesquioxide of chromium, &c. In these processes of reduction the sulphur separates in the form of a fine white powder. Whether the hydrosulphuric acid had better be applied in the gaseous form or in aqueous solution depends always upon the special circumstances of the case.

## III. Bases and Metals.

### § 33.

Bases are divided into oxygen bases and sulphur bases. The former result from the combination of metals or of compound radicals of similar character with oxygen, the latter from the combination of the same bodies with sulphur.

The *oxygen bases* are classified into alkalies, alkaline earths, earths proper, and oxides of the heavy metals. The alkalies are readily soluble in water; the alkaline earths dissolve with greater difficulty in that menstruum; and magnesia, the last member of the class, is only very sparingly soluble in it. The earths proper and the oxides of the heavy metals are insoluble in water or nearly so (except protoxide of thallium). The solutions of the alkalies and alkaline earths are caustic when sufficiently concentrated; they have an alkaline taste, change the yellow color of turmeric paper to brown, and restore the blue tint of reddened litmus paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colors, whilst those with weak acids generally have an alkaline reaction. The earths proper and the oxides of the heavy metals combine likewise with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The *sulphur bases* resulting from the combination of the metals of the alkalies and alkaline earths with sulphur are soluble in water. The solutions have a strong alkaline reaction. The other sulphur bases do not dissolve in water. All sulphur bases form with sulphur acids sulphur salts.

## *a.* Oxygen Bases.

### α. Alkalies.

### § 34.

### 1. Potassa (K O) and Soda (Na O).

The preparation of perfectly pure potassa or soda is a difficult opera-
n. It is advisable therefore to prepare, besides perfectly pure caustic
tali, also some which is not quite pure, and some which being free
m certain impurities may in many cases be safely substituted for the
re substance.

*a. Common solution of soda.*—Put into a clean cast-iron pan provided
th a lid 3 parts of crystallized carbonate of soda of commerce and 15
rts of water, heat to boiling, and add, in small portions at a time,
ick milk of lime prepared by pouring 3 parts of warm water over 1
rt of quicklime, and letting the mixture stand in a covered vessel
ıtil the lime is reduced to a uniform pulpy mass. Keep the liquid in
e pan boiling whilst adding the milk of lime, and for a quarter of an
ur longer, then filter off a small portion, and try whether the filtrate
ill causes effervescence in hydrochloric acid. If this is the case, the
iling must be continued, and if necessary some more milk of lime
ust be added to the fluid. When the solution is perfectly free from
rbonic acid, cover the pan, allow the fluid to cool a little, and then
aw off the nearly clear solution from the residuary sediment, by
eans of a siphon filled with water, and transfer it to a glass flask.
oil the residue a second and a third time with water, and draw off the
uid in the same way. Cover the flask close with a glass plate, and
low the lime suspended in the fluid to subside completely. Scour the
n pan clean, pour the clear solution back into it, and evaporate it to
or 7 parts. The solution so prepared contains from 9 to 10 per cent.
soda, and has a specific gravity of from 1·13 to 1·15. If it is wished
filter a solution of soda which is not quite clear, a covered funnel
ould be used, which has been charged first with lumps of white
arble and then with powder of the same, the fine dust being rinsed
t with water before the filter is used (Graeger). Solution of soda
ust be clear, colorless, and as free as possible from carbonic acid;
lphide of ammonium must not impart a black color to it. Traces of
icic acid, alumina, and phosphoric acid are usually found in a solution
soda prepared in this manner; on which account it is unfit for use in
curate experiments. Solution of soda is kept best in bottles closed
th ground glass caps. In default of capped bottles, common ones
th well-ground stoppers may be used, in which case the neck must be
ped perfectly dry and clean inside and the stopper coated with paraffin;
ıce, if this precaution is neglected, it will be found impossible after a
ne to remove the stopper, particularly if the bottle is only rarely opened.

*b. Hydrate of potassa purified with alcohol.*—Dissolve some caustic
tassa of commerce in rectified spirit of wine in a stoppered bottle by
gestion and shaking; let the fluid stand, decant it, or filter it if
cessary, and evaporate the clear fluid in a silver dish over the gas or
irit lamp until no *more vapors escape*; adding from time to time,
*ring the evaporation, some water to* prevent blackening of the mass.
*ce the silver dish in cold water* until it has sufficiently cooled;
r.

remove the cake of caustic potassa from the dish, break it into coarse lumps in a hot mortar, and keep in a well-closed glass bottle. When required for use, dissolve a small lump in water.

The hydrate of potassa so prepared is sufficiently pure for most purposes; it contains, indeed, a minute trace of alumina, but is usually free from phosphoric acid, sulphuric acid, and silicic acid. The solution must remain clear upon addition of sulphide of ammonium; hydrochloric acid must only produce a barely perceptible effervescence in it. The solution acidified with hydrochloric acid must, upon evaporation to dryness, leave a residue which dissolves in water to a clear fluid. The solution acidified with hydrochloric acid, and then mixed with ammonia in the least possible excess, must not show any flocks of alumina, at least until it has stood in a warm place for several hours. The solution acidified with nitric acid must not give any precipitate with a nitric acid solution of molybdate of ammonia.

*c. Hydrate of potassa prepared with baryta.*—Dissolve pure crystals of baryta (§ 36) by heating with water, and add to the solution pure sulphate of potassa until a portion of the filtered fluid, acidified with hydrochloric acid and diluted, no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of sulphate of potassa). Let the turbid fluid clear, decant, and evaporate in a silver dish as in *b*. The hydrate of potassa so prepared is perfectly pure, except that it contains a trifling admixture of sulphate of potassa, which is left behind upon dissolving the hydrate in a little water. This hydrate is but rarely required, its use being in fact exclusively confined to the detection of minute traces of alumina.

*Uses.*—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the so precipitated oxides redissolve in an excess of the precipitant, as, for instance, alumina, sesquioxide of chromium, and oxide of lead; whilst others remain undissolved, *e.g.* sesquioxide of iron, teroxide of bismuth, &c. The fixed alkalies serve therefore also as a means to separate the former from the latter. Potassa and soda dissolve also many salts (*e.g.* chromate of lead), sulphur compounds, &c., and contribute thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action of potassa or soda exhibit peculiar colors, or possess other characteristic properties that may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitates of hydrate of protoxide of manganese, hydrate of protoxide of iron, suboxide of mercury, &c. The fixed alkalies expel ammonia from its salts, and enable us thus to detect that body by its smell, its action on vegetable colors, &c.

## § 35.

### 2. Ammonia. *Oxide of Ammonium.* ($NH_4O$).

*Preparation.*—Ammonia is generally prepared in cast-iron vessels on a large scale, and it will be found more economical to buy it.* For preparing it on a small scale the following method answers well.

* *An excellent receipt* for preparing ammonia in rather large quantities will be *found in Zeitschrift f.* anal. Chem. 1, 186.

Introduce into a flask 4 parts of chloride of ammonium, either crystallized or in lumps, and the dry hydrate of lime prepared from 5 parts of quicklime, mix by shaking, and cautiously add enough water to make the powder agglomerate into lumps. Set the flask in a sand bath and connect it with a rather large wash bottle and delivery tube. Put a small quantity of water in the wash bottle, and about 10 parts of water in the flask destined to absorb the gas. Place the latter in cold water, and then begin to apply heat. Evolution of gas speedily sets in. Continue to heat until no more bubbles appear. Open the cork of the flask to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver is perfectly pure; dilute it with water until the specific gravity is about 96 = 10 per cent. of ammonia. Keep the fluid in bottles closed with ground stoppers.

*Tests.*—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated in a platinum dish. When heated with an equal volume of lime water, it should cause no turbidity, at least not to a very marked extent (carbonic acid). When supersaturated with nitric acid, neither solution of nitrate of baryta nor of nitrate of silver must render it turbid, nor must sulphuretted hydrogen impart to it the slightest color.

*Uses.*—Solution of ammonia, although formed by conducting ammoniacal gas ($NH_3$) into water, and letting that gas escape upon exposure to the air, and much quicker when heated, may also be regarded as a solution of oxide of ammonium ($NH_4O$) in water, the first acceding equivalent of water (HO) being assumed to form $NH_4O$ with $NH_3$. Upon this assumption solution of ammonia may accordingly be looked upon as an analogous fluid to solution of potassa and solution of soda, which greatly simplifies the explanation of all its reactions, the oxygen salts resulting from the neutralization of oxygen acids by solution of ammonia being also assumed to contain oxide of ammonium $NH_4O$, instead of $NH_3$. Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in an excess of ammonia, as, for instance, the oxides of zinc, cadmium, silver, copper, &c., whilst others are insoluble in free ammonia. This reagent may therefore serve also to separate and distinguish the former from the latter. Some of these precipitates, as well as their solutions in ammonia, exhibit peculiar colors, which may at once lead to the detection of the individual metal which they respectively contain.

Many of the oxides which are precipitated by ammonia from neutral solutions are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the ammonia salt formed in the process. Compare § 53.

## β. Alkaline Earths.

### § 36.

### 1. Baryta (BaO).

*Preparation.*—*There are a great many ways of preparing hydrate of baryta; but as witherite is now easily and cheaply procurable, I prefer*

the following method to all others: Mix intimately together 100 parts of finely pulverized witherite, 10 parts of charcoal in powder, and 5 parts of resin, put the mixture in an earthenware pot, put on the lid and lute it on with clay, and expose the pot so prepared to the heat of a brick-kiln. Break and triturate the baked mass, boil repeatedly with water in an iron pot, filter into vessels, stopper, and let them stand in the cold, when large quantities of crystals of hydrate of baryta (Ba O, H O + 8 aq.) will make their appearance. Let the crystals drain in properly covered funnels, dry rapidly between sheets of blotting paper, and keep them in well closed bottles. For use dissolve 1 part of the crystals in 20 parts of water, with the aid of heat, and filter the solution. The baryta water so prepared is purer than the mother liquor running off from the crystals. The residue, which is insoluble in water and consists of undecomposed witherite and charcoal, is turned to account in the preparation of chloride of barium.

*Tests.*—Baryta water must, after precipitation of the baryta by pure sulphuric acid, give a filtrate remaining clear when mixed with spirit of wine, and leaving no fixed residue upon evaporation in a platinum crucible.

*Uses.*—Caustic baryta, being a strong base, precipitates the earths and metallic oxides insoluble in water from the solutions of their salts. In the course of analysis we use it simply to precipitate magnesia. Baryta water may also be used to precipitate those acids which form insoluble compounds with this base; it is applied with this view to effect the detection of carbonic acid, the removal of sulphuric acid, phosphoric acid, &c.

## § 37.

## 2. Lime (Ca O).

We use—

*a. Hydrate of lime. b. Lime water.*

The former is obtained by slacking pure calcined lime in lumps, in a porcelain dish, with half its weight of water. The heat which accompanies the combination of the lime and the water is sufficient to evaporate the excess of water. Hydrate of lime must be kept in a well-stoppered bottle.

To prepare lime water, digest hydrate of lime for some time with cold distilled water, shaking the mixture occasionally; let the undissolved portion of lime subside, decant, and keep the clear fluid in a well-stoppered bottle. If it is wished to have the lime water quite free from all traces of alkalies, baryta and strontia, which are almost invariably present in hydrate of lime prepared from calcined limestone, the liquids of the first two or three decantations must be removed, and the fluid decanted afterwards alone made use of.

*Tests.*—Lime water must impart a strongly-marked brown tint to turmeric paper, and give a not too inconsiderable precipitate with carbonate of soda. It speedily loses these properties upon exposure to the air, and is thereby rendered totally unfit for analytical purposes.

*Uses.*—Lime forms with many acids insoluble, with others soluble salts. Lime water may therefore serve to distinguish the former acids, which it precipitates from their solutions, from the latter, which it will *of course fail to precipitate.* Many of the precipitable acids are thrown *down only under* certain conditions, *e.g.* on boiling (citric acid), which

affords a ready means of distinguishing between them by altering these conditions. We use lime water in analysis principally to effect the detection of carbonic acid, and also to distinguish between citric acid and tartaric acid. Hydrate of lime is chiefly used to liberate ammonia from ammonia salts.

### γ. Heavy Metals and their Oxides.

§ 38.

#### 1. Zinc (Zn).

Select zinc of good quality and, above all, perfectly free from arsenic. The method described § 132, 10 will serve to detect the presence of the slightest trace of this substance. Fuse the metal and pour it in a thin stream into a large vessel with water. Zinc which contains arsenic must be absolutely rejected, for no process of purification known to us that can in any way pretend to simplicity will ever succeed in removing every trace of that metal (Eliot and Storer).*

*Uses.*—Zinc serves in qualitative analysis for the evolution of hydrogen, and also of arsenetted and antimonetted hydrogen gases (compare § 131, 10, and § 132, 10); it is occasionally used also to precipitate some metals from their solutions; in which process the zinc simply displaces the other metal ($CuO, SO_3 + Zn = ZnO, SO_3 + Cu$). Zinc is also sometimes used for the detection of sulphurous acid and phosphorous acid;. it must then be tested for sulphide of zinc or phosphide of zinc, as the case may be, see §§ 139 and 148.

#### 2. Iron (Fe).

Iron reduces many metals and precipitates them from their solutions in the metallic state. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

#### 3. Copper (Cu).

We use copper exclusively to effect the reduction of mercury, which precipitates upon it as a white coating shining with silvery lustre when rubbed. A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

§ 39.

#### 4. Hydrate of Teroxide of Bismuth ($BiO_3, HO$).†

*Preparation.*—Dissolve bismuth, freed from arsenic by fusion with hepar sulphuris, in dilute nitric acid; dilute the solution till a slight permanent precipitate is produced; filter and evaporate the filtrate

* According to Gunning (Scheikundige Bijdragen, Deel I. Nr. 1, p. 113), the purification may be effected by repeated fusion with a mixture of carbonate of soda and sulphur.

† *The basic nitrate of teroxide of bismuth* of commerce, if perfectly free from arsenic *and antimony, may also be used instead of* the hydrated teroxide.

to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, and dry the white precipitate, and keep it for use.

*Tests.*—The hydrate of bismuth is dissolved in dilute nitric acid and precipitated with sulphuretted hydrogen. Part of the precipitated sulphide is treated with ammonia and filtered, part is treated with sulphide of ammonium and filtered. The filtrates are then mixed with hydrochloric acid in excess; the first should give no precipitate, the second only a white precipitate of sulphur.

*Uses.*—Teroxide of bismuth when boiled with alkaline solutions of metallic sulphides decomposes with the latter, giving rise to the formation of metallic oxides and sulphide of bismuth. It is better adapted to effect decompositions of this kind than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is complete or not. It has still another advantage over oxide of copper, viz., it does not, like the latter, dissolve in the alkaline fluid in presence of organic substances; nor does it act as a reducing agent upon reducible oxygen compounds. We use it principally to convert tersulphide and pentasulphide of arsenic into arsenious and arsenic acids, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of suboxide.

### *b.* Sulphur Bases.

### § 40.

### 1. Sulphide of Ammonium ($NH_4S$).

We use in analysis—

*a. Colorless protosulphide of ammonium.*

*b. Yellow polysulphide of ammonium.*

*Preparation.*—Transmit hydrosulphuric acid gas through 3 parts of solution ammonia until no further absorption takes place; then add 2 parts more of the same solution of ammonia. The action of hydrosulphuric acid upon ammonia gives rise to the formation, first, of $NH_4S$ ($NH_4O$ and $HS = NH_4S$ and $HO$), then of $NH_4S$, $HS$; upon addition of the same quantity of solution of ammonia as has been saturated, the ammonia decomposes with the hydrosulphate of sulphide of ammonium, and protosulphide of ammonium is formed, thus: $NH_4S, HS + NH_4O = 2\,NH_4S + HO$. The rule, however, is to add only two-thirds of the quantity of solution of ammonia, as it is better the preparation should contain a little hydrosulphate of sulphide of ammonium than that free ammonia should be present. To employ, as has usually been the case hitherto, hydrosulphate of sulphide of ammonium instead of the simple protosulphide is unnecessary, and simply tends to increase the smell of sulphuretted hydrogen in the laboratory, as the preparation allows that gas to escape when in contact with metallic sulphur acids.

Sulphide of ammonium should be kept in well-corked phials. It is colorless at first, and deposits no sulphur upon addition of acids. Upon *exposure to the air,* however, it acquires a yellow tint, owing to the *formation of bisulphide* of ammonium, which is attended also with

formation of ammonia and water, thus: $2\,NH_4S + O = NH_4S_2 + NH_3 + HO$. Continued action of the oxygen of the air upon the sulphide of ammonium tends at first to the formation of still higher sulphides; but afterwards the fluid deposits sulphur, and finally all the sulphide of ammonium is decomposed and the solution contains nothing but ammonia and hyposulphite of ammonia. The formation of hyposulphite is thus explained: $NH_4S_2 + O_3 = NH_4O,S_2O_2$.

The sulphide of ammonium which has turned yellow by moderate exposure to the air may be used for all purposes requiring the employment of yellow sulphide of ammonium. The yellow sulphide may also be expeditiously prepared by digesting the protosulphide with some sulphur. All kinds of yellow sulphide of ammonium deposit sulphur and look turbid and milky on being mixed with acids.

*Tests.*—Sulphide of ammonium must strongly emit the odor peculiar to it; with acids it must evolve abundance of sulphuretted hydrogen; the evolution of gas may be attended by the separation of a pure white precipitate, but no other precipitate must be formed. Upon evaporation and exposure to a red heat in a platinum dish it must leave no residue. It must not even on heating precipitate or render turbid solution of magnesia or solution of lime (carbonate of ammonia or free ammonia).

*Uses.*—Sulphide of ammonium is one of the most frequently employed reagents. It serves (*a*) to effect the precipitation of those metals which hydrosulphuric acid fails to throw down from acid solutions, *e.g.* of iron, cobalt, &c. ($NH_4S + FeO,SO_3 = FeS + NH_4O,SO_3$); (*b*) to separate the metallic sulphides thrown down from acid solutions by hydrosulphuric acid, since it dissolves some of them to sulphur salts, as, for instance, the sulphides of arsenic and antimony, &c. ($NH_4S$, $AsS_3$, &c.), whilst leaving others undissolved—for instance, sulphide of lead, sulphide of cadmium, &c. The sulphide of ammonium used for this purpose must contain an excess of sulphur if the metallic sulphides to be dissolved will dissolve only as higher sulphides, as, for instance SnS, which dissolves with ease only as $SnS_2$.

From solutions of salts of alumina and sesquioxide of chromium sulphide of ammonium precipitates hydrates of these oxides, with escape of sulphuretted hydrogen, as the sulphur compounds corresponding to these oxides cannot form in the wet way. [$Al_2O_3, 3SO_3 + 3NH_4S + 6HO = Al_2O_3, 3HO + 3(NH_4O,SO_3) + 3HS$]. Salts insoluble in water are thrown down by sulphide of ammonium unaltered from their solutions in acids; thus, for instance, phosphate of lime is precipitated unaltered from its solution in hydrochloric acid.

## § 41.

### 2. Sulphide of Sodium (NaS).

*Preparation.*—Same as sulphide of ammonium, except that solution of soda is substituted for solution of ammonia. Filter, if necessary, and keep the fluid obtained in well-stoppered bottles. If required to contain some higher sulphide of sodium digest it with powdered sulphur.

*Uses.*—Sulphide of sodium must be substituted for sulphide of ammonium to effect the *separation of sulphide* of copper from sulphur *compounds soluble in alkaline sulphides, e.g.* from protosulphide of tin, as *sulphide of copper is not quite insoluble* in sulphide of ammonium.

## IV. Salts.

Of the many salts employed as reagents those of potassa, soda, and ammonia are used principally on account of their acids; salts of soda may therefore often be substituted for the corresponding potassa salts, &c. Thus it is almost always a matter of perfect indifference whether we use carbonate of soda or carbonate of potassa, ferrocyanide of potassium or ferrocyanide of sodium, &c. I have therefore here classified the salts of the alkalies *by their acids*. With the salts of the alkaline earths and those of the oxides of the heavy metals the case is different; these are not used for their acid, but for their base; we may therefore often substitute for one salt of a base another similar one, as *e.g.* nitrate or acetate of baryta for chloride of barium, &c. For this reason I have classified the salts of the alkaline earths and of the heavy metals *by their bases*.

### *a.* Salts of the Alkalies.

§ 42.

#### 1. Sulphate of Potassa ($KO, SO_3$).

*Preparation.*—Purify sulphate of potassa of commerce by recrystallization, and dissolve 1 part of the pure salt in 12 parts of water.

*Uses.*—Sulphate of potassa serves to detect and separate baryta and strontia. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 43.

#### 2. Phosphate of Soda ($2NaO, HO, PO_5 + 24$ aq.).

*Preparation.*—Purify phosphate of soda of commerce by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

*Tests.*—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it must completely, and without effervescence, redissolve upon addition of dilute nitric acid.

*Uses.*—Phosphate of soda precipitates the alkaline earths and all heavy metallic oxides by double affinity. It serves in the course of analysis, after the separation of the oxides of the heavy metals, as a test for alkaline earths in general; and, after the separation of baryta, strontia, and lime, as a special test for the detection of magnesia; for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating as basic phosphate of magnesia and ammonia.

§ 44.

#### 3. Oxalate of Ammonia ($2NH_4O, C_4O_6 + 2$ aq.).

*Preparation.*—Dissolve 1 part of commercial oxalic acid (which usually contains potassa) in 6 parts of boiling water, allow to cool, *pour off or filter the* solution from the crystals of oxalic acid, which *generally contain* quadroxalate of potassa, evaporate again and allow to

cool. The second crop of crystals is practically free from potassa. A third crop equally pure may also be obtained. The mother liquor together with the first crop may be used in the preparation of oxalate of potassa or soda. Dissolve the pure oxalic acid in 2 parts of distilled water, with the aid of heat, add solution of ammonia until the reaction is distinctly alkaline, and put the vessel in a cold place. Let the crystals drain. The mother liquor will, upon proper evaporation, give another crop of crystals. Purify all the crystals by recrystallization. Dissolve 1 part of the pure salt in 24 parts of water for use.

*Tests.*—The solution of oxalate of ammonia must not be precipitated nor rendered turbid by hydrosulphuric acid, nor by sulphide of ammonium. Ignited on platinum, the salt must volatilize without leaving a residue.

*Uses.*—Oxalic acid forms with lime, strontia, baryta, oxide of lead, and other metallic oxides, insoluble or very difficultly soluble compounds; oxalate of ammonia produces therefore in the aqueous solutions of the salts of these bases precipitates of the corresponding oxalates. In analysis it serves principally for the detection and separation of lime.

## § 45.

### 4. Acetate of Soda ($NaO, C_4H_3O_3 + 6$ aq., or $NaO, \bar{A} + 6$ aq.).

*Preparation.*—Dissolve crystallized carbonate of soda in a little water, add to the solution acetic acid to slight excess, evaporate to crystallization, and purify the salt by recrystallization. For use dissolve 1 part of the salt in 10 parts of water.

*Tests.*—Acetate of soda must be colorless and free from empyreumatic matter and inorganic acids.

*Uses.*—The stronger acids in the free state decompose acetate of soda, combining with the base, and setting the acetic acid free. In the course of analysis acetate of soda is used principally to precipitate phosphate of sesquioxide of iron (which is insoluble in acetic acid) from its solution in hydrochloric acid. It serves also to effect the separation of sesquioxide of iron and alumina, which it precipitates on boiling from the solutions of their salts.

## § 46.

### 5. Carbonate of Soda ($NaO, CO_2 + 10$ aq.).

*Preparation.*—Take bicarbonate of soda of commerce, put the powder into a funnel stopped loosely with cotton wool, make the surface even, cover it with a disk of difficultly permeable paper with turned-up edges, and wash by pouring small quantities of water on the paper disk, until the filtrate, acidified with nitric acid, is not rendered turbid by solution of nitrate of silver, nor by solution of chloride of barium. Let the salt dry, and then convert it by gentle ignition into the simple carbonate. This is effected best in a crucible or dish of silver or platinum; but it may be done also in a perfectly clean vessel of cast iron, or, on a small scale, in a porcelain dish. Pure carbonate of soda may be obtained also by repeated recrystallization of carbonate of soda of commerce. *For use dissolve 1 part of the anhydrous salt or 2·7 parts of the crystallized salt in 5 parts of water.*

*Tests.*—Carbonate of soda must be perfectly white. Its solution, after supersaturation with nitric acid, must not be rendered turbid by chloride of barium or nitrate of silver; nor must addition of sulphocyanide of potassium impart a red, or warming with molybdate of ammonia and nitric acid a yellow tint to it, or give a yellow precipitate; the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, must leave no residue (silicic acid) when redissolved in water. When fused in a glass tube with cyanide of potassium for a long time in a current of carbonic acid, it should give no trace of a dark sublimate (arsenic). See § 132, 12.

*Uses.*—With the exception of the alkalies, carbonate of soda precipitates the whole of the bases in the form of neutral or basic carbonates. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of soda exhibit a characteristic color, which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of soda serves also for the decomposition of many insoluble salts of the alkaline earths or of the metals, more particularly of those with organic acids. Upon boiling with carbonate of soda these salts are converted into insoluble carbonates, whilst the acids combine with the soda and are thus obtained in solution. Carbonate of soda is often used also to saturate free acids.

## § 47.

### 6. Carbonate of Ammonia ($NH_4O, CO_2$).

*Preparation.*—We use purified sesquicarbonate of ammonia entirely free from any smell of animal oil, such as is prepared on a large scale from a mixture of chloride of ammonium and carbonate of lime by sublimation. The outer and the inner surface of the mass are carefully scraped. One part of the salt is dissolved by digestion with 4 parts of water to which one part of solution of caustic ammonia has been added.

*Tests.*—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of baryta nor of nitrate of silver, nor sulphuretted hydrogen, must color or precipitate it, after supersaturation with nitric acid.

*Uses.*—Carbonate of ammonia precipitates, like carbonate of soda, most metallic oxides and earths; it is generally employed in preference to the latter reagent, because it introduces no non-volatile body into the solution. Complete precipitation of many of the oxides takes place also only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner carbonate of ammonia dissolves many hydrated oxides and sulphides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions many oxides which it precipitates from neutral solutions. (Compare § 53.) We use carbonate of ammonia in analysis principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia; also to *separate sulphide of* arsenic, which is soluble in it, from sulphide of *antimony, which is* insoluble.

## § 48.

### 7. Bisulphite of Soda ($NaO,HO,2SO_2$).

*Preparation.*—Heat 5 parts of copper clippings with 20 parts of concentrated sulphuric acid in a flask, and conduct the sulphurous acid gas evolved, first through a washing bottle containing some water, then into a flask containing 4 parts of purified bicarbonate of soda (§ 46), or 7 parts of pure crystallized carbonate of soda, and from 20 to 30 parts of water, and which is not much more than half full; continue the transmission of the gas until the evolution of carbonic acid ceases. Keep the solution, which smells strongly of sulphurous acid, in a well-stoppered bottle.

*Tests.*—Sulphite of soda, when evaporated to dryness with pure sulphuric acid, must leave a residue,* the aqueous solution of which is not altered by hydrosulphuric acid, nor precipitated yellow by heating with a solution of molybdate of ammonia mixed with nitric acid.

*Uses.*—Sulphurous acid has a great tendency to pass to the state of sulphuric acid by absorbing oxygen. It is therefore one of our most powerful reducing agents. Sulphite of soda, which has the advantage of being less readily decomposed than sulphurous acid, acts in an analogous manner upon addition of acid. We use it principally to reduce arsenic acid to arsenious acid, chromic acid to sesquioxide of chromium, and sesquioxide of iron to protoxide. It will serve also to effect the separation of tersulphide of arsenic, which is soluble in it, from the sulphides of antimony and tin, which are insoluble in this reagent.

## § 49.

### 8. Nitrite of Potassa ($KO,NO_3$).

*Preparation.*—In an iron pan fuse 1 part of nitre, add 2 parts of lead, and keep stirred with an iron rod. Even at a low red heat the lead becomes for the most part oxidized and converted into a yellow powder. To oxidize the remainder, the heat is increased to visible redness and maintained at that point for half an hour Allow to cool, treat with cold water, filter and pass carbonic acid through the filtrate. This precipitates almost the whole of the lead in solution, the remainder is removed with a little sulphuretted hydrogen. Evaporate the clear fluid to dryness, finally with stirring, and fuse in order to destroy any hyposulphite of potassa (Aug. Stromeyer). When required, dissolve 1 part in 2 parts of water, neutralize cautiously with acetic acid, and filter.

*Tests.*—Nitrite of potassa must upon addition of dilute sulphuric acid copiously evolve nitric oxide gas.

*Uses.*—Nitrite of potassa is an excellent means to effect the detection and separation of cobalt, in the solutions of which metal it produces a precipitate of nitrite of potassa and sesquioxide of cobalt. It serves also in presence of free acid to liberate iodine from its compounds.

* The evaporation is attended with copious evolution of sulphurous acid.

§ 50.

### 9. Bichromate of Potassa ($KO, 2CrO_3$).

*Preparation.*—Purify the salt of commerce by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

*Uses.*—Chromate of potassa decomposes most of the soluble salts of metallic oxides by double affinity. Most of the precipitated chromates are very sparingly soluble, and many of them exhibit characteristic colors which lead readily to the detection of the particular metal which they respectively contain. We use bichromate of potassa principally as a test for lead.

§ 51.

### 10. Granular Antimonate of Potassa ($KO,SbO_5 + 7$ aq.).

*Preparation.*—Project a mixture of equal parts of pulverized tartar-emetic and nitrate of potassa in small portions at a time into a red-hot crucible. After the mass has deflagrated, keep it at a moderate red heat for a quarter of an hour longer, which will make it froth at first, but after some time it will be seen in a state of calm fusion. Remove the crucible now from the fire, let the mass get sufficiently cold, and then extract it with warm water. Transfer to a suitable vessel, which is easily done by rinsing, and decant the supernatant clear fluid from the heavy white powder deposited. Concentrate the decanted fluid by evaporation. After 1 or 2 days a doughy mass will separate. Treat this mass with three times its volume of cold water, working it at the same time with a spatula. This operation will serve to convert it into a fine granular powder, to which add the powder from which the fluid was decanted, wash well with boiling water, till the washings cease to be alkaline, and dry on blotting paper. 100 parts of tartar-emetic give about 36 parts of antimonate of potassa (Brunner).

*Tests* and *Uses.*—Granular antimonate of potassa is very sparingly soluble in water, requiring 90 parts of boiling and 250 parts of cold water for solution. The solution had always best be prepared immediately before required for use, by boiling the salt with water, and filtering off the fluid from the undissolved portion. The solution must be clear and of neutral reaction; it must give no precipitate with solution of chloride of potassium, nor with solution of chloride of ammonium; but solution of chloride of sodium must produce a crystalline precipitate in it. Antimonate of potassa is a valuable reagent for soda, but its employment requires great caution, see § 90.

§ 52.

### 11. Molybdate of Ammonia ($NH_4O,MoO_3$), dissolved in Nitric Acid.

*Preparation.*—Triturate sulphide of molybdenum with about an equal bulk of coarse quartz sand washed with hydrochloric acid, until the mass is reduced to a moderately fine powder; heat the powder to faint redness, with repeated stirring, until the mass has acquired a lemon-yellow color (which after cooling turns whitish). With small quantities this

operation may be conducted in a flat platinum dish, with large quantities in a muffle. Extract the residuary mass with solution of ammonia, filter, evaporate the filtrate, heat the residue to faint redness until the mass appears yellow or white, and then digest for several days with nitric acid in the water bath, in order to convert the phosphoric acid which is almost invariably present in the ore to the tribasic state. When the nitric acid is evaporated dissolve the residue in 4 parts of solution of ammonia, filter rapidly, and pour the filtrate into 15 parts by weight of nitric acid of 1·20 specific gravity. Keep the mixture standing several days in a moderately warm place, which will cause the separation of any remaining traces of phosphoric acid as phospho-molybdate of ammonia. Decant the colorless fluid from the precipitate, and keep it for use. Heated to 40° no white precipitate (molybdic acid or an acid salt of the same) will separate; but if the temperature is raised beyond that point this will at once take place unless more nitric acid be added (EGGERTZ).

*Uses.*—Phosphoric acid and arsenic acid form with molybdic acid and ammonia peculiar yellow compounds which are almost absolutely insoluble in the nitric acid solution of molybdate of ammonia. The phosphoric acid compound is formed in the cold, the arsenic acid compound requires heat. Molybdate of ammonia affords therefore an excellent means to detect these acids, and more especially very minute quantities of phosphoric acid in acid solutions containing sesquioxide of iron, alumina, and alkaline earths.

## § 53.

### 12. CHLORIDE OF AMMONIUM ($NH_4Cl$).

*Preparation.*—Select sublimed white sal ammoniac of commerce. If it contains iron it must be purified. For this purpose add ammonia to the boiling solution, continue boiling till the alkaline reaction has almost gone, allow the precipitate to subside, filter, and crystallize. Dissolve 1 part of the salt in 8 parts of water for use.

*Tests.*—Solution of chloride of ammonium must leave no fixed residue upon evaporation on a platinum knife. Sulphide of ammonium must have no action upon it. Its reaction must be perfectly neutral.

*Uses.*—Chloride of ammonium serves principally to retain in solution certain oxides (*e.g.* protoxide of manganese, magnesia) or salts (*e.g.* tartrate of lime) upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of chloride of ammonium is based upon the tendency of the ammonia salts to form double compounds with other salts. Chloride of ammonium serves also to distinguish between precipitates possessed of similar properties; for instance, to distinguish the basic phosphate of magnesia and ammonia, which is insoluble in chloride of ammonium, from other precipitates of magnesia. It is used also to precipitate from their solutions in potassa various substances which are soluble in that alkali, but insoluble in ammonia; *e.g.* alumina, sesquioxide of chromium, &c. In this process the elements of the chloride of ammonium transpose with those of the potassa, and chloride of potassium, water, and ammonia are formed. Chloride of ammonium is applied also as a special reagent to effect the precipitation of platinum as ammonio-bichloride of platinum.

## § 54.

### 13. Cyanide of Potassium (K Cy).

*Preparation.*—Heat ferrocyanide of potassium of commerce (perfectly free from sulphate of potassa) gently, with stirring, until the crystallization water is completely expelled; triturate the anhydrous mass, and mix 8 parts of the dry powder with 3 parts of perfectly dry carbonate of potassa; fuse the mixture in a covered Hessian or, better still, in a covered iron crucible, until the mass is in a faint glow, appears clear, and a sample of it, taken out with a heated glass or iron rod, looks perfectly white. Remove the crucible now from the fire, tap it gently, and let it cool a little until the evolution of gas has ceased; pour the fused cyanide of potassium into a heated tall, crucible-shaped vessel of clean iron or silver, or into a moderately hot Hessian crucible, with proper care, to prevent the running out of any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible. Let the mass now slowly cool in a somewhat warm place. The cyanide of potassium so prepared is exceedingly well adapted for analytical purposes, although it contains carbonate and cyanate of potassa; which latter is upon solution in water transformed into carbonate of ammonia and carbonate of potassa ($K O, C_2 N O + 4 H O = K O, C O_2 + N H_4 O, C O_2$). Keep it in the solid form in a well-stoppered bottle, and dissolve 1 part of it in 4 parts of water, without application of heat, when required for use.

*Tests.*—Cyanide of potassium must be of a milk-white color and quite free from particles of iron or charcoal. It must completely dissolve in water to a clear fluid. It must contain neither silicic acid nor sulphide of potassium; the precipitate which salts of lead produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid,* must completely dissolve in water to a clear fluid.

*Uses.*—Cyanide of potassium prepared in the manner described produces in the solutions of most of the salts of metallic oxides precipitates of cyanides of metals or of oxides or carbonates which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore by further addition of the reagent be separated from the oxides or carbonates which are insoluble in cyanide of potassium. Some of the metallic cyanides redissolve invariably in the cyanide of potassium as double cyanides, even in presence of free hydrocyanic acid and upon boiling; whilst others combine with cyanogen to new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are cobalticyanide of potassium and ferro- and ferricyanide of potassium. These differ from the double cyanides of the other kind particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may accordingly serve also to separate the metals which form compounds of the latter description from others the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis this reagent is of great importance, as it serves to

* *This supersaturation with hydrochloric acid is attended with disengagement of hydrocyanic acid.*

effect the separation of cobalt from nickel; also that of copper, the sulphide of which metal is soluble in it, from cadmium, the sulphide of which is insoluble.

§ 55.

14. FERROCYANIDE OF POTASSIUM ($2\,K,C_6N_3Fe + 3$ aq. = $2\,K,Cfy + 3$ aq.).

*Preparation.*—The ferrocyanide of potassium is found in commerce sufficiently pure. 1 part of the salt is dissolved in 12 parts of water for use.

*Uses.*—Ferrocyanogen forms with most metals compounds insoluble in water, which frequently exhibit highly characteristic colors. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing places with the metals. Ferrocyanide of copper and ferrosesquicyanide of iron exhibit the most characteristic colors of all; ferrocyanide of potassium serves therefore particularly as a test for oxide of copper and sesquioxide of iron.

§ 56.

15. FERRICYANIDE OF POTASSIUM ($3\,K, C_{12}N_6Fe_2 = 3\,K,Cfdy$).

*Preparation.*—Conduct chlorine gas slowly into a solution of 1 part of ferrocyanide of potassium in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep red color by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate in a solution of sesquichloride of iron, but imparts a brownish tint to it. Evaporate the fluid now in a dish to $\frac{1}{4}$ of its weight, and let crystallize. The mother liquor will upon further evaporation yield a second crop of crystals equally fit for use as the first. Dissolve the whole of the crystals obtained in 3 parts of water, filter if necessary; evaporate the solution briskly to half its volume, and let crystallize again. Whenever required for use, dissolve a few of the crystals, which are of a splendid red color, in a little water. The solution, as already remarked, must produce neither a blue precipitate nor a blue color in a solution of sesquichloride of iron.

*Uses.*—Ferricyanide of potassium decomposes with solutions of metallic oxides in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides the ferriprotocyanide of iron is more particularly characterized by its color, and we apply ferricyanide of potassium therefore principally as a test for protoxide of iron.

§ 57.

16. SULPHOCYANIDE OF POTASSIUM ($K,C_2N\,S_2$ or $K,\,Cy\,S_2$).

*Preparation.*—Mix together 46 parts of anhydrous ferrocyanide of potassium, 17 parts of carbonate of potassa, and 32 parts of sulphur; introduce the mixture into an iron pan provided with a lid, and fuse over a gentle fire; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now,

towards the end of the operation, to faint redness, in order to decompose the hyposulphite of potassa which has been formed in the process. Remove the half refrigerated and still soft mass from the pan, crush it, and boil repeatedly with alcohol of from 80 to 90 per cent. Upon cooling, part of the sulphocyanide of potassium will separate in colorless crystals; to obtain the remainder, distil the alcohol from the mother liquor. Dissolve 1 part of the salt in 10 parts of water for use.

*Tests.*—Solution of sulphocyanide of potassium must remain perfectly colorless when mixed with perfectly pure dilute hydrochloric acid.

*Uses.*—Sulphocyanide of potassium serves for the detection of sesquioxide of iron, for which substance it is at once the most characteristic and the most delicate test.

### *b.* Salts of the Alkaline Earths.

### § 58.

### 1. Chloride of Barium ($BaCl + 2$ aq.).

*Preparation.—a. From heavy spar.* Mix together 8 parts of pulverized sulphate of baryta, 2 parts of charcoal in powder, and 1 part of common resin. Put the mixture in a crucible, and expose it in a wind furnace to a long-continued red heat. Triturate the crude sulphide of barium obtained, boil about $\frac{9}{10}$ of the powder with 4 times its quantity of water, and add hydrochloric acid until all effervescence of sulphuretted hydrogen has ceased, and the fluid manifests a slight acid reaction. Add now the remaining $\frac{1}{10}$ part of the sulphide of barium, boil some time longer, then filter, and let the alkaline fluid crystallize. Dry the crystals, redissolve them in water, and crystallize again.

*b. From witherite.* Pour 10 parts of water upon 1 part of pulverized witherite, and gradually add crude hydrochloric acid until the witherite is almost completely dissolved. Add now a little more finely pulverized witherite, and heat, with frequent stirring, until the fluid has entirely or very nearly lost its acid reaction; add solution of sulphide of barium as long as a precipitate forms; then filter, evaporate the filtrate to crystallization, and purify by crystallizing again. For use dissolve 1 part of the chloride of barium in 10 parts of water.

*Tests.*—Pure chloride of barium must not alter vegetable colors; its solution must not be colored or precipitated by hydrosulphuric acid, nor by sulphide of ammonium. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent leaves not the slightest residue when evaporated on platinum foil.

*Uses.*—Baryta forms with many acids soluble, with others insoluble compounds. This property of baryta affords us therefore a means of distinguishing the former acids, which are not precipitated by chloride of barium, from the latter, in the solution of the salts of which this reagent produces a precipitate. The precipitated salts of baryta severally show with acids a different deportment. By subjecting these salts to the action of acids we are therefore enabled to subdivide the group of *precipitable* acids and even to detect certain individual acids. This *makes chloride of* barium one of our most important reagents to distin-

guish between certain groups of acids, and more especially also to effect the detection of sulphuric acid.

§ 59.

2. NITRATE OF BARYTA ($BaO, NO_5$).

*Preparation.*—Treat carbonate of baryta, no matter whether witherite or precipitated by carbonate of soda from solution of sulphide of barium, with dilute nitric acid free from chlorine, and proceed exactly as directed in the preparation of chloride of barium from witherite. For use, dissolve 1 part of the salt in 15 parts of water.

*Tests.*—Solution of nitrate of baryta must not be made turbid by solution of nitrate of silver. Other tests the same as for chloride of barium.

*Uses.*—Nitrate of baryta is used instead of chloride of barium in cases where it is desirable to avoid the presence of a metallic chloride in the fluid.

§ 60.

3. CARBONATE OF BARYTA ($BaO, CO_2$).

*Preparation.*—Dissolve crystallized chloride of barium in water, heat to boiling, and add a solution of carbonate of ammonia mixed with some caustic ammonia, or of pure carbonate of soda, as long as a precipitate forms; let the precipitate subside, decant five or six times, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of nitrate of silver. Stir the precipitate with water to the consistence of thick milk, and keep this mixture in a stoppered bottle. It must of course be shaken every time it is required for use.

*Tests.*—Pure sulphuric acid must precipitate every fixed particle from a solution of carbonate of baryta in hydrochloric acid (compare § 36).

*Uses.*—Carbonate of baryta completely decomposes the solutions of many metallic oxides, *e.g.* sesquioxide of iron, alumina; precipitating from them the whole of the oxide as hydrate and basic salt, whilst some other metallic salts are not precipitated by it. It serves therefore to separate the former from the latter, and affords an excellent means of effecting the separation of sesquioxide of iron and alumina from protoxide of manganese, oxide of zinc, lime, magnesia, &c. It must be borne in mind, however, that the salts must not be sulphates, as carbonate of baryta equally precipitates the latter bases from these compounds.

§ 61.

4. SULPHATE OF LIME ($CaO, SO_3$, *crystallized* $CaO, SO_3 + 2$ aq.).

*Preparation.*—Digest and shake powdered crystallized gypsum (selenite) for some time with water; let the undissolved portion subside, decant, and keep the clear fluid for use.

*Uses.*—Sulphate of lime, being a difficultly soluble salt, is a convenient agent in cases where it is wished to apply a solution of a lime salt or of a sulphate of a definite degree of dilution. As dilute solution of

a lime salt it is used for the detection of oxalic acid; whilst as dil solution of a sulphate it affords an excellent means of distinguish between baryta, strontia, and lime.

§ 62.

5. Chloride of Calcium (Ca Cl, *crystallized* Ca Cl + 6 aq.).

*Preparation.*—Dilute 1 part of crude hydrochloric acid with 6 p of water, and add to the fluid marble or chalk until the last por added remains undissolved; add now some hydrate of lime, then phuretted hydrogen water until a filtered portion of the mixture is longer altered by sulphide of ammonium. Then let the mixture st covered for 12 hours at a gentle heat; filter, exactly neutralize filtrate, concentrate by evaporation, and crystallize. Let the cry drain, and dissolve 1 part of the salt in 5 parts of water for use.

*Tests.*—Solution of chloride of calcium must be perfectly neutral, neither be colored nor precipitated by sulphide of ammonium; nor ou it to evolve ammonia when mixed with hydrate of potassa or hydrat lime.

*Uses.*—Chloride of calcium is in its action and application analog to chloride of barium. For as the latter reagent is used to separate inorganic acids into groups, so chloride of calcium serves in the s manner to effect the separation of the organic acids into groups, sin precipitates some of them, whilst it forms soluble compounds with oth And, as is the case with the baryta precipitates, the different condit under which the various insoluble lime salts are thrown down enabl to subdivide the group of precipitable acids.

§ 63.

6. Sulphate of Magnesia.

(Mg O, $S O_3$, *crystallized* Mg O, $S O_3$, H O + 6 aq.).

*Preparation.*—Dissolve 1 part of sulphate of magnesia of commer 10 parts of water; if the salt is not perfectly pure, subject it to rec tallization.

*Tests.*—Sulphate of magnesia must have a neutral reaction. Its s tion, when mixed with a sufficient quantity of chloride of ammoni must, after the lapse of half an hour, not appear clouded or tinge pure ammonia, or by carbonate or oxalate of ammonia, or by sulphid ammonium.

*Uses.*—Sulphate of magnesia serves almost exclusively for the de tion of phosphoric acid and arsenic acid, which it precipitates f aqueous solutions of phosphates and arsenates, in presence of amm and chloride of ammonium, in the form of almost absolutely insol highly characteristic double salts (basic phosphate or basic arsenat magnesia and ammonia). Sulphate of magnesia is also employed to sulphide of ammonium (see § 40).

### c. Salts of the Oxides of the Heavy Metals.

### § 64.

### 1. Sulphate of Protoxide of Iron.

(Fe O, $S O_3$, *crystallized* Fe O, $S O_3$, H O + 6 aq.).

*Preparation.*—Heat an excess of iron nails free from rust, or of clean iron wire, with dilute sulphuric acid until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals with water very slightly acidulated with sulphuric acid, dry, and keep for use. The sulphate of protoxide of iron may also be prepared from the solution of sulphide of iron in dilute sulphuric acid which is obtained in the process of evolving hydrosulphuric acid.

*Tests.*—The crystals of sulphate of protoxide of iron must have a fine pale green color. Crystals that have been more or less oxidized by the action of the air, and give a brownish-yellow solution when treated with water, leaving undissolved basic sulphate of sesquioxide of iron behind, must be altogether rejected. Hydrosulphuric acid must not precipitate solution of sulphate of protoxide of iron after addition of some hydrochloric acid, nor even impart a blackish tint to it.

*Uses.*—Sulphate of protoxide of iron has a great disposition to absorb oxygen, and to be converted into the sulphate of the sesquioxide. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which it separates nitric oxide by withdrawing three atoms of oxygen from it. The decomposition of the nitric acid being attended in this case with the formation of a very peculiar brownish-black compound of nitric oxide with an undecomposed portion of the salt of the protoxide of iron, this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Sulphate of protoxide of iron serves also for the detection of hydroferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of that metal.

### § 65.

### 2. Sesquichloride of Iron ($Fe_2Cl_3$).

*Preparation.*—Heat in a flask a mixture of 10 parts of water and 1 part of pure hydrochloric acid with small iron nails until no further evolution of hydrogen is observed, even after adding the nails in excess; filter the solution into another flask, and conduct into it chlorine gas, with frequent shaking, until the fluid no longer produces a blue precipitate in solution of ferricyanide of potassium. Heat until the excess of chlorine is expelled. Dilute until the fluid is twenty times the weight of the iron dissolved, and keep for use.

*Tests.*—Solution of sesquichloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a diluted sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be *proved by the formation* of a precipitate which shaking *the vessel or agitating the fluid fails* to redissolve. Ferricyanide of *potassium must not impart a blue color* to it.

*Uses.*—Sesquichloride of iron serves to subdivide the group of org acids which chloride of calcium fails to precipitate, as it produces cipitates in solutions of benzoates and succinates, but not in cold s tions of acetates and formates. The aqueous solutions of the ne acetate and formate of sesquioxide of iron exhibit an intensely red c sesquichloride of iron is therefore a useful agent for detecting a acid and formic acid. Sesquichloride of iron is exceedingly adapted to effect the decomposition of phosphates of the alkaline e (see § 142). It serves also for the detection of hydroferrocyanic with which it produces Prussian blue.

§ 66.

### 3. Nitrate of Silver ($AgO.NO_5$).

*Preparation.*—Dissolve 1 part of the pure salt in 20 parts of wa

*Tests.*—Dilute hydrochloric acid must completely precipitate all particles from solution of nitrate of silver, which should have a ne reaction; the fluid filtered from the precipitated chloride of silver accordingly leave no residue when evaporated on a watch-glass, must be neither precipitated nor colored by hydrosulphuric acid.

*Uses.*—Oxide of silver forms with many acids soluble, with ot insoluble compounds. Nitrate of silver may therefore serve, chloride of barium, to effect the separation and arrangement of into groups.

Most of the insoluble compounds of silver dissolve in dilute n acid; chloride, bromide, iodide, and cyanide, ferrocyanide, ferricya and sulphide of silver are insoluble in that menstruum. Nitra silver is therefore a most excellent agent to distinguish and sep from all other acids the hydracids corresponding to the last enume compounds of silver. Many of the insoluble salts of silver exhi peculiar color (chromate of silver, arsenate of silver), or manife characteristic deportment with other reagents or upon the applicati heat (formate of silver); nitrate of silver is therefore an impo agent for the positive detection of certain acids.

§ 67.

### 4. Acetate of Lead ($PbO, \bar{A}$, *crystallized* $PbO, \bar{A} + 3$ aq.)

The best acetate of lead of commerce is sufficiently pure; for dissolve 1 part of the salt in 10 parts of water.

*Tests.*—Sugar of lead must completely dissolve in water acid with one or two drops of acetic acid; the solution must be quite and colorless; hydrosulphuric acid must throw down all fixed part from it. On mixing the solution of sugar of lead with carbona ammonia in excess, and filtering the mixture, the filtrate must show a bluish tint (copper).

*Uses.*—Oxide of lead forms with a great many acids compound soluble in water, which are marked either by peculiarity of col *characteristic deportment.* The acetate of lead therefore produces *cipitates in the solutions* of these acids or of their salts, and essent *contributes to the* detection of several of them. Thus chromate of

for instance, is characterized by its yellow color, phosphate of lead by its peculiar deportment before the blowpipe, and malate of lead by its ready fusibility.

§ 68.

5. NITRATE OF SUBOXIDE OF MERCURY ($Hg_2O, NO_5$, *crystallized* $Hg_2O, NO_5 + 2$ aq.).

*Preparation.*—Pour 1 part of pure nitric acid of 1·2 spec. gr. on 1 part of pure mercury in a porcelain dish, and let the vessel stand twenty-four hours in a cool place; separate the crystals formed from the undissolved mercury and the mother liquor, and dissolve them in water mixed with one-sixteenth part of nitric acid, by trituration in a mortar. Filter the solution, and keep the filtrate in a bottle with some metallic mercury covering the bottom of the vessel.

*Tests.*—The solution of nitrate of suboxide of mercury must give with dilute hydrochloric acid a copious white precipitate of subchloride of mercury; hydrosulphuric acid must produce no precipitate in the fluid filtered from this, or at all events only a trifling black precipitate (sulphide of mercury).

*Uses.*—Nitrate of suboxide of mercury acts in an analogous manner to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and, in the second place, it serves for the detection of several readily oxidizable bodies, *e.g.* of formic acid, as the oxidation of such bodies, which takes place at the expense of the oxygen of the suboxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 69.

6. CHLORIDE OF MERCURY (Hg Cl).

The chloride of mercury of commerce is sufficiently pure. For use dissolve 1 part of the salt in 16 parts of water.

*Uses.*—Chloride of mercury gives with several acids, *e.g.* with hydriodic acid, peculiarly colored precipitates, and may accordingly be used for the detection of these acids. It is an important agent for the detection of tin where that metal is in solution in the state of protochloride; if only the smallest quantity of that compound is present the addition of chloride of mercury in excess to the solution is followed by separation of subchloride of mercury insoluble in water. In a similar manner chloride of mercury serves also for the detection of formic acid.

§ 70.

7. SULPHATE OF COPPER (Cu O, $SO_3$, *crystallized* Cu O, $SO_3$, H O + 4 aq.).

*Preparation.*—This reagent may be obtained in a state of great purity from the residue remaining in the flask in the process of preparing bisulphite of soda (§ 48), by treating with water, applying heat, filtering, adding a few drops of nitric acid, boiling for some time, allowing to crystallize, and purifying the salt by recrystallization. For use dissolve 1 part in 10 parts of water.

*Tests.—After precipitation by hydrosulphuric acid, ammonia and sulphide of ammonium must leave the filtrate unaltered.*

*Uses.*—Sulphate of copper is employed in qualitative analysis to effect the precipitation of hydriodic acid in the form of subiodide of copper. For this purpose it is necessary to mix the solution of 1 part of sulphate of copper with 2½ parts of sulphate of protoxide of iron, otherwise half of the iodine will separate in the free state. The protoxide of iron changes in this process to sesquioxide, at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used also for the detection of arsenious and arsenic acids; it serves likewise as a test for the soluble ferrocyanides.

## § 71.

### 8. Protochloride of Tin ($SnCl$, *crystallized* $SnCl + 2$ aq.).

*Preparation.*—Reduce grain tin to powder by means of a file, or by fusing it in a small porcelain dish, removing from the fire, and triturating with a pestle until it has passed again to the solid state. Boil the powder for some time with concentrated hydrochloric acid in a flask (taking care always to have an excess of tin in the vessel) until hydrogen gas is scarcely evolved; dilute the solution with 4 times the quantity of water slightly acidulated with hydrochloric acid, and filter. Keep the filtrate for use in a well-stoppered bottle containing small pieces of metallic tin, or some pure tin-foil. If these precautions are neglected the protochloride will soon change to bichloride, with separation of white oxychloride, which will render the reagent unfit for use.

*Tests.*—Solution of protochloride of tin must, when added to excess of solution of chloride of mercury, immediately produce a white precipitate of subchloride of mercury; when treated with hydrosulphuric acid it must give a dark brown precipitate; it must not be precipitated nor rendered turbid by sulphuric acid.

*Uses.*—The great tendency of protochloride of tin to absorb oxygen and thus to form binoxide, or rather bichloride—as the binoxide in the moment of its formation decomposes with the free hydrochloric acid present—makes this substance one of our most powerful reducing agents. It is more particularly suited to withdraw part or the whole of the chlorine from chlorides. We employ it in the course of analysis as a test for mercury; also to effect the detection of gold.

## § 72.

### 9. Bichloride of Platinum ($PtCl_2$, *crystallized* $PtCl_2 + 10$ aq.).

*Preparation.*—Treat platinum clippings, purified by boiling with nitric acid, with concentrated hydrochloric acid and some nitric acid in a narrow-necked flask, and apply a very gentle heat, adding occasionally fresh portions of nitric acid, until the platinum is completely dissolved. Evaporate the solution on the water-bath, with addition of hydrochloric acid, and dissolve the semifluid residue in 10 parts of water for use.

*Tests.*—Bichloride of platinum must, upon evaporation to dryness in the water-bath, leave a residue which dissolves completely in spirit or wine.

*Uses.*—*Bichloride* of platinum forms very sparingly soluble double *salts with chloride of* potassium and chloride of ammonium, but not

with chloride of sodium; it serves therefore to detect ammonia and potassa, and may, indeed, be looked upon as our most delicate reagent for the latter substance in the wet way.

§ 73.

### 10. Sodio-Protochloride of Palladium ($NaCl, PdCl$).

Dissolve 5 parts of palladium in nitrohydrochloric acid (comp. § 72), add 6 parts of pure chloride of sodium, evaporate in the water-bath to dryness, and dissolve 1 part of the residuary double salt in 12 parts of water for use. The brownish solution affords an excellent means for detecting and separating iodine.

§ 74.

### 11. Terchloride of Gold ($AuCl_3$).

*Preparation.*—Take fine shreds of gold, which may be alloyed with silver or copper, treat them in a flask with nitrohydrochloric acid in excess, and apply a gentle heat until no more of the metal dissolves, then dilute the solution with 10 parts of water. If the gold was alloyed with copper—which is known by the brownish-red precipitate produced by ferrocyanide of potassium in a portion of the solution diluted with water—mix it with solution of sulphate of protoxide of iron in excess. This will reduce the terchloride to metallic gold, which will separate in the form of a fine brownish-black powder; wash the powder in a small flask, and redissolve it in nitrohydrochloric acid; evaporate the solution on the water-bath, and dissolve the residue in 30 parts of water. If the gold was alloyed with silver, the latter metal remains as chloride upon treating the alloy with nitrohydrochloric acid. In that case evaporate the solution at once, and dissolve the residue in water for use.

*Uses.*—Terchloride of gold has a great tendency to yield up its chlorine; it therefore readily converts protochlorides into higher chlorides, protoxides, with the co-operation of water, into higher oxides. These oxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis this reagent is used only for the detection of protoxide of tin, in the solutions of which it produces a brownish-red or purple color or precipitate.

## V. Coloring Matters and Indifferent Vegetable Substances.

§ 75.

### 1. Test Papers.

#### a. Blue Litmus Paper.

*Preparation.*—Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the one half by repeatedly stirring with *a glass rod dipped in very dilute* sulphuric acid, until the color of *the fluid just appears red; add now* the other half of the blue filtrate, pour

the whole fluid into a dish, and draw slips of fine unsized paper through it; suspend these slips over threads, and leave them to dry. The color of litmus paper must be uniform, and neither too light nor too dark. The paper must be readily wetted by aqueous fluids.

*Uses.*—The red coloring matters contained in litmus appear blue in the commercial article, in the aqueous extract of the same, and in the paper colored with it, only from the presence of alkaline bases. If any one of the blue preparations comes in contact with free acid, the latter combines with the bases, and in consequence the proper color of the natural litmus appears. Litmus paper is therefore an excellent means for the detection of free acids. The power of weak volatile acids to bind the alkaline bases is but transient; hence when they volatilize the blue color again appears. It must be borne in mind that the soluble neutral salts of most of the heavy metals also cause the blue color to change to red.

### β. Reddened Litmus Paper.

*Preparation.*—Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Dip slips of paper in the solution, and dry them as in α. The dried slips must look distinctly red.

*Uses.*—Alkalies and alkaline earths, and also the sulphides of their metals, alkaline carbonates, and the soluble salts of some other weak acids, especially of boracic acid, all present bases to the red coloring matters of litmus and occasion the formation of blue compounds similar to those contained in blue litmus. Hence the reddened litmus is colored blue by the solutions of these substances, and it serves for their detection in general. Ammonia does not color litmus paper permanently blue, so on its volatilization the natural red color of the litmus reappears.

### γ. Georgina Paper (*Dahlia Paper*).

*Preparation.*—Boil the violet-colored petals of *Georgina purpurea* (purple dahlia) in water, or digest them with spirit of wine, and dip slips of paper in the tincture obtained. The latter should be neither more nor less concentrated than is necessary to make the paper when dry again appear of a fine and light violet blue color. Should the color too much incline to red, this may be remedied by adding a very little ammonia to the tincture.

*Uses.*—Georgina paper is reddened by acids, whilst alkalies impart a beautiful green tint to it. It is therefore an extremely convenient substitute both for the blue and the reddened litmus paper. This reagent, if properly prepared, is a most delicate test both for acids and alkalies. Concentrated solutions of caustic alkalies turn Georgina paper yellow by destroying the coloring matter.

### δ. Turmeric Paper.

*Preparation.*—Digest and heat 1 part of bruised turmeric root with 6 parts of weak spirit of wine, filter the tincture obtained, and dip slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint; they must be readily wetted by aqueous fluids.

*Uses.*—Turmeric paper serves the same as reddened litmus paper and dahlia paper for the detection of free alkalies, &c., as they change its yellow color to brown. It is not so delicate as the other test papers; but the change of color is highly characteristic, and is very distinctly perceptible with many colored fluids; we therefore cannot well dispense with this paper. When testing with turmeric paper it is to be borne in mind that, besides the substances enumerated in $\beta$, other bodies (boracic acid, for instance) possess the property of turning its yellow color to red, more especially on drying. It affords an excellent means for the detection of boracic acid.

All test papers are cut into slips, which are kept in small well-closed boxes, or in bottles covered with black paper, as continued action of light destroys the color.

### 2. Solution of Indigo.

*Preparation.*—Take from 4 to 6 parts of fuming sulphuric acid, add slowly and in small portions at a time 1 part of finely-pulverized indigo, taking care to keep the mixture well stirred. The acid at first acquires a brownish tint from the coloring matter mixed with the indigo blue, but it subsequently turns deep blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo blue is thereby destroyed; it is therefore advisable when dissolving large quantities of the substance to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into 20 times the quantity of water, mix, filter, and keep the filtrate for use.

*Uses.*—Indigo is decomposed by boiling with nitric acid, yellow-colored oxidation products being formed. It serves therefore for the detection of nitric acid. Solution of indigo is also well adapted to effect the detection of chloric acid and of free chlorine.

## B. REAGENTS IN THE DRY WAY.

## I. Fluxes and Decomposing Agents.

### § 76.

### 1. Mixture of Carbonate of Soda and Carbonate of Potassa ($NaO, CO_2 + KO, CO_2$).

*Preparation.*—Digest 10 parts of purified bitartrate of potassa in powder with 10 parts of water and 1 part of hydrochloric acid for several hours on the water-bath, with frequent stirring; put the mass into a funnel with a small filter in the point; let it drain; cover with a disc of rather difficultly permeable filtering paper with upturned edges, and wash by repeatedly pouring upon this small quantities of cold water; continue this washing process until the fluid running off is no longer rendered turbid by solution *of nitrate* of silver, after addition of nitric acid. *Dry the bitartrate of potassa* freed in this manner from lime (and *phosphoric acid). It is now necessary* to prepare pure nitrate of potassa.

To effect this, dissolve nitrate of potassa of commerce in half its weight of boiling water, filter the solution into a porcelain or stoneware dish, using a hot funnel, and stir it well with a clean wooden or porcelain spatula until cold. Transfer the crystalline powder to a funnel loosely stopped with cotton wool, let it drain, press down tight, make even at the top, cover with a double disc of difficultly permeable filtering paper with upturned edges, and pour upon this at proper intervals small portions of water until the washings are no longer made turbid by solution of nitrate of silver. Empty now the contents of the funnel into a porcelain dish, dry in this vessel, and reduce the mass to a fine powder.

Mix now 2 parts of the pure bitartrate of potassa with 1 part of the pure nitrate of potassa; project the perfectly dry mixture in small portions at a time into a clean-scoured cast-iron pot heated to gentle redness; when the mixture has deflagrated heat strongly until a sample gives with water a perfectly colourless solution. Triturate the charred mass with water, filter, wash slightly, and evaporate the filtrate in a porcelain or, better still, in a silver dish, until the fluid is covered with a persistent pellicle. Let the mixture now cool, with constant stirring; put the crystals of carbonate of potassa on a funnel, let them well drain, wash slightly, dry thoroughly in a silver or porcelain dish, and keep in a well-stoppered bottle. The mother liquor leaves upon evaporation a salt which, though containing traces of alumina and silicic acid, may still be turned to account for many purposes.

Mix 13 parts of the pure carbonate of potassa prepared in the manner just now described with 10 parts of pure anhydrous carbonate of soda, and keep the mixture in a well-stoppered bottle. The mixture of carbonate of potassa and carbonate of soda may also be prepared by deflagrating 20 parts of pure bitartrate of potassa with 9 parts of pure nitrate of soda, treating with water, and evaporating the solution to dryness. Or by igniting pure tartrate of potassa and soda, extracting the carbonaceous mass with water, and evaporating the clear solution to dryness.

*Tests.*—The purity of the mixed salt is tested as directed § 46. To detect any trace of cyanide of potassium that may happen to be present, add a little of a solution of proto-sesquioxide of iron, then hydrochloric acid in excess, when the bluish-green coloration of the fluid and the formation of a blue precipitate after a time will indicate the presence of cyanide of potassium.

*Uses.*—If silicic acid or a silicate is fused with about 4 parts (consequently with an excess) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate hydrochloric acid separates the silicic acid as hydrate. If a fixed alkaline carbonate is fused together with sulphate of baryta, strontia, or lime, there are formed carbonates of the alkaline earths and sulphate of the alkali, in which new compounds both the base and the acid of the originally insoluble salt may now be readily detected. However, we do not use either carbonate of potassa or carbonate of soda separately to effect the decomposition of the insoluble silicates and sulphates; but we *apply for this purpose* the above-described mixture of both, because this *mixture requires* a far lower degree of heat for fusion than either of its

two components, and thus enables us to conduct the operation over a Berzelius lamp, or over a simple gas-lamp. The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 77.

2. Hydrate of Baryta (Ba O, HO).

*Preparation.*—The crystals of baryta prepared in the manner directed § 36 are heated gently in a silver or platinum dish, until the water of crystallization is completely expelled. The residuary white mass is pulverized, and kept for use in a well-closed bottle.

*Uses.*—Hydrate of baryta fuses at a gentle red heat without losing its water. Upon fusing silicates which resist decomposition by acids together with about 4 times their weight of hydrate of baryta, basic silicates are formed which acids will decompose. If, therefore, the fused mass is treated with water and hydrochloric acid, the solution evaporated to dryness, and the residue digested with dilute hydrochloric acid, the silicic acid is left behind, and the oxides are obtained in solution in the form of chlorides. We use hydrate of baryta as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of baryta, since it does not require a very high temperature for its fusion, as is the case with the carbonate, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the nitrate. The operation of fusing with hydrate of baryta is conducted in silver or platinum crucibles.

§ 78.

3. Fluoride of Calcium (Ca F).

Take fluor-spar as pure as can be procured and, more particularly, free from alkalies, reduce to fine powder, and keep this for use.

*Uses.*—Fluoride of calcium applied in conjunction with sulphuric acid serves to effect the decomposition of silicates insoluble in acids, and more especially to detect the alkalies which they contain. Compare Section III. *Silicic acid*, § 150.

§ 79.

4. Nitrate of Soda ($Na O, NO_5$).

*Preparation.*—Neutralize pure nitric acid with pure carbonate of soda exactly, and evaporate to crystallization. Dry the crystals thoroughly, triturate, and keep the powder for use.

*Tests.*—A solution of nitrate of soda must not be made turbid by solution of nitrate of silver or nitrate of baryta, nor precipitated by carbonate of soda.

*Uses.*—Nitrate of soda serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated with them. We use this reagent principally *to convert* several metallic sulphides, and more *particularly the sulphides of tin*, antimony, and arsenic, into oxides *and acids; also to effect the rapid* and complete combustion of organic

substances. For the latter purpose, however, nitrate of ammonia is sometimes preferable; it is prepared by saturating nitric acid with carbonate of ammonia.

§ 80.

### 5. Acid Sulphate of Potassa ($KO, HO, 2SO_3$).

*Preparation.*—Mix 87 parts neutral sulphate of potassa (§ 42) with 49 parts pure concentrated sulphuric acid in a platinum dish or large platinum crucible, heat to low redness till the mass is in a state of calm fusion, then pour out into a platinum dish placed in cold water, or onto a piece of porcelain, break the cake into smaller pieces and keep for use.

*Tests.*—The acid sulphate of potassa must dissolve in water with ease to a clear fluid with a strong acid reaction. The solution must not be rendered turbid or precipitated by hydrosulphuric acid or by ammonia and sulphide of ammonium.

*Uses.*—The acid sulphate of potassa at the temperature of fusion dissolves and decomposes many bodies, which cannot be dissolved and decomposed by acids in the wet way without considerable difficulty, such as ignited alumina, titanic acid, chrome ironstone, &c. This, reagent therefore, is of service in effecting the solution or decomposition of such bodies. The fusion is preferably effected in platinum vessels.

## II. Blowpipe Reagents.

§ 81.

### 1. Carbonate of Soda ($NaO, CO_2$).

*Preparation.*—See § 46.

*Uses.*—Carbonate of soda serves, in the first place, to promote the reduction of oxidized substances in the inner flame of the blowpipe. In fusing it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. With salts of the heavy metals the reduction is preceded by separation of the base. It co-operates in this process also chemically by the transposition of its constituents (according to R. Wagner, in consequence of the formation of cyanide of sodium). Where the quantity operated upon was very minute, the reduced metal is often found in the pores of the charcoal. In such cases the parts surrounding the cavity which contained the substance are dug out with a knife, and triturated in a small mortar; the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small spangles, as the case may be.

Carbonate of soda serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. A few only of the bases dissolve in fusing carbonate of soda, but acids dissolve in it with facility. Carbonate of soda is also applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly-formed sulphate of soda being reduced at the same time to sulphide of sodium; and to effect the decomposition of sulphide of arsenic, with which it forms a double sulphide of arsenic and sodium, and arsenite or arsenate of soda, thus converting it to a state

which permits its subsequent reduction by hydrogen. Carbonate of soda also is the most sensitive reagent in the dry way for the detection of manganese, as it produces when fused in the outer flame with a substance containing manganese a green opaque bead, owing to the formation of manganate of soda.

§ 82.

2. CYANIDE OF POTASSIUM (K Cy).

*Preparation.*—See § 54.

*Uses.*—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from many sulphur compounds. This reduction is attended in the former case with formation of cyanate of potassa, by the absorption of oxygen, and in the latter case with formation of sulphocyanide of potassium, by the taking up of sulphur. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce metallic antimony from antimonious acid or from sulphide of antimony, metallic iron from sesquioxide of iron, &c. The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit or gas lamp. Cyanide of potassium is a most valuable and important agent to effect the reduction of binoxide of tin, antimonic acid, and more particularly of tersulphide of arsenic. Cyanide of potassium is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like binoxide of tin, the reduction of which by means of carbonate of soda requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blowpipe experiments we invariably use a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended here to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has moreover this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 83.

3. BIBORATE OF SODA. *Borax.*

($NaO, 2BO_3$, *crystallized* + 10 aq.).

The purity of commercial borax may be tested by adding to its solution carbonate of soda or, after previous addition of nitric acid, solution of nitrate of baryta or of nitrate of silver. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible, until

it ceases to swell; it is then left to cool, and afterwards pulverized and kept for use.

*Uses.*—Boracic acid manifests a great affinity for oxides when brought into contact with them in a state of fusion. This affinity enables it, in the first place, to combine directly with oxides; secondly, to expel weaker acids from their salts; and, thirdly, to predispose metals, sulphides, and haloid compounds to oxidize in the outer flame of the blowpipe, that it may combine with the oxides. Most of the thus produced borates fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or by the formation of double salts. Now in the biborate of soda we have both free boracic acid and borate of soda; the union of these two substances renders it one of our most important blowpipe reagents. In the process of fusing with borax we usually select platinum wire for a support; the loop of the wire is moistened or heated to redness, then dipped into the powder, and exposed to the outer flame; a colorless bead of fused borax is thus produced. A small portion of the substance is then attached to the bead, by bringing the latter into contact with it whilst still hot or having previously moistened it. The bead with the substance adhering to it is now exposed to the gas or blowpipe flame, and the reactions are observed. The following points ought to be more particularly watched :—(1) Whether or not the substance dissolves to a transparent bead, and whether or not the bead retains its transparency on cooling; (2) whether the bead exhibits a distinct color, which in many cases at once clearly indicates the individual metal which the substance contains; as is the case, for instance, with cobalt; and (3) whether the bead manifests the same or a different deportment in the outer and in the inner flame. Reactions of the latter kind arise from the ensuing reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

## § 84.

### 4. Phosphate of Soda and Ammonia. *Microcosmic Salt.*

$(NaO, NH_4O, HO, PO_5$, *crystallized* $+ 8$ aq.).

*Preparation.*—*a.* Heat to boiling 6 parts of phosphate of soda and 1 part of pure chloride of ammonium with 2 parts of water, and let the solution cool. Free the crystals produced of the double phosphate of soda and ammonia from the chloride of sodium which adheres to them by recrystallization, with addition of some solution of ammonia. Dry the purified crystals, pulverize, and keep for use.

*b.* Take 2 equal parts of pure tribasic phosphoric acid, and add solution of soda to the one, solution of ammonia to the other, until both fluids have a distinct alkaline reaction; mix the two together, and let the mixture crystallize.

*Tests.*—Phosphate of soda and ammonia dissolves in water to a fluid with feebly alkaline reaction. The yellow precipitate produced in this fluid by nitrate of silver must completely dissolve in nitric acid. Upon fusion on a platinum wire, microcosmic salt must give a clear and colorless bead.

*Uses.*—On heating phosphate of soda and ammonia the ammonia

escapes with the water of crystallization, leaving acid pyrophosphate of soda ($Na\,O, H\,O, P\,O_2$); upon heating more strongly the last equivalent of water escapes likewise, and readily fusible metaphosphate of soda ($Na\,O, P\,O_5$) is left behind. The action of microcosmic salt is quite analogous to that of biborate of soda. We prefer it, however, in some cases to borax as a solvent or flux, the beads which it forms with many substances being more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

## § 85.

### 5. Nitrate of Protoxide of Cobalt ($CoO, NO_5$, *crystallized* + 5 aq.).

*Preparation.*—Fuse in a Hessian crucible 3 parts of acid sulphate of potassa, and add to the fused mass, in small portions at a time, 1 part of well-roasted cobalt ore (the purest zaffre you can procure) reduced to fine powder. The mass thickens, and acquires a pasty consistence. Heat now more strongly until it has become more fluid again, and continue to apply heat until the excess of sulphuric acid is *completely* expelled, and the mass accordingly no longer emits white fumes. Remove the fused mass now from the crucible with an iron spoon or spatula, let it cool, and reduce it to powder; boil this with water until the undissolved portion presents a soft mass; then filter the rose-red solution, which is free from arsenic and nickel, and mostly also from iron. Add to the filtrate a small quantity of carbonate of soda, so as to throw down a little carbonate of protoxide of cobalt, boil, and filter. Precipitate the solution, which is now free from iron, boiling with carbonate of soda, wash the precipitate well, and treat it still moist with oxalic acid in excess. Wash the rose-red oxalate of protoxide of cobalt thoroughly, dry, and heat to redness in a glass tube, in a current of hydrogen gas. This decomposes the oxalate into carbonic acid, which escapes, and metallic cobalt, which is left behind. Wash the metal, first with water containing acetic acid, then with pure water, dissolve in dilute nitric acid, treat—if necessary—with hydrosulphuric acid, filter the fluid from the sulphide of copper, &c., which may precipitate, evaporate the solution in the water-bath to dryness, and dissolve 1 part of the residue in 10 parts of water for use.

*Tests.*—Solution of nitrate of protoxide of cobalt must be free from other metals, and especially also from salts of the alkalies; when precipitated with sulphide of ammonium, and filtered, the filtrate must upon evaporation on platinum leave no fixed residue.

*Uses.*—Protoxide of cobalt forms upon ignition with certain infusible bodies (oxide of zinc, alumina) peculiarly coloured compounds, and may accordingly serve for their detection.

# SECTION III.

## REACTIONS, OR DEPORTMENT OF BODIES WITH REAGENTS.

### § 86.

I STATED in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the unknown constituents of any given compound into forms of which we know the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the several constituents of which the analysed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us any the wiser if we do not know the language in which the answer is returned, so in like manner will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the substance examined.

Before we can therefore proceed to enter upon the practical investigation of analytical chemistry, it is indispensable that we should really possess the most perfect knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances we wish to analyse. Now this perfect knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds and the manifestation of the various reactions; and in the second place, in a distinct impression of the color, form, and physical properties which characterize the new compound. This section of the work demands therefore not only the most careful and attentive study, but requires moreover that the student should examine and verify by actual experiment every fact asserted in it.

The method usually adopted in elementary works on chemistry is to treat of the various substances and their deportment with reagents individually and separately, and to point out their characteristic reactions. I have, however, in the present work deemed it more judicious and better adapted to its elementary character, to arrange those substances which are in many respects analogous into groups, and thus, by comparing their analogies with their differences, to place the latter in the clearest possible light.

### A.—DEPORTMENT OF THE METALLIC OXIDES AND OF THEIR RADICALS.

### § 87.

Before proceeding to the special study of the several metallic oxides, I give here a general view of the whole of them classified in groups—

showing which oxides belong to each group. The grounds upon which the classification has been arranged will appear from the special consideration of the several groups.

First group—

*Potassa, soda, ammonia* (oxide of cæsium, oxide of rubidium, lithia).

Second group—

*Baryta, strontia, lime, magnesia.*

Third group—

*Alumina, sesquioxide of chromium* (berylla, thoria, zirconia, yttria, oxide of erbium, oxides of cerium, lanthanium, didymium, titanium, tantalium, niobium).

Fourth group—

Oxides of *zinc, manganese, nickel, cobalt, iron* (of uranium, thallium, indium, vanadium).

Fifth group—

Oxides of *silver, mercury, lead, bismuth, copper, cadmium* (of palladium, rhodium, osmium, ruthenium).

Sixth group—

Oxides and acids of *gold, platinum, tin, antimony, arsenic* (of iridium, molybdenum, tellurium, tungsten, selenium).

Of these metallic oxides only those printed in italics are found distributed extensively and in large quantities in that portion of the earth's crust which is accessible to our investigations; these are therefore most important to chemistry, arts and manufactures, agriculture, pharmacy, &c.; and we shall therefore dwell upon them at greater length. The remainder are more briefly considered in paragraphs printed in smaller type, which may be passed over by the younger class of students of analytical chemistry. The properties and reactions of the metals themselves I have given only in the case of those that are more frequently met with in the metallic state in analytical operations.

## § 88.

### FIRST GROUP.

More common oxides:—Potassa, Soda, Ammonia.

Rarer oxides:—Oxide of Cæsium, Oxide of Rubidium, Lithia.

*Properties of the group.*—The alkalies are readily soluble in water, as well in the pure or caustic state as in the form of sulphides, carbonates, and phosphates. (The salts of lithia, however, dissolve with difficulty.) Accordingly the alkalies do not precipitate one another in the pure state, nor as carbonates or phosphates (which in the case of lithia, however, presupposes a higher degree of dilution of the solutions), nor are they precipitated by hydrosulphuric acid under any condition whatever. The solutions of the pure alkalies as well as of their sulphides and carbonates restore the blue color of reddened litmus-paper, and impart an intensely brown tint to turmeric paper.

*Special Reactions of the more common Oxides of the first group.*

§ 89.

*a.* POTASSA (KO).

1. POTASSA and its HYDRATE and SALTS are not volatile at a faint red-heat. Potassa and its hydrate deliquesce in the air; the oily liquids formed absorb carbonic acid rapidly from the air, but without solidifying.

2. Nearly the whole of the SALTS OF POTASSA are soluble in water Those with colorless acids are colorless. The neutral salts of potassa with strong acids do not alter vegetable colors. Carbonate of potassa crystallizes (in combination with 2 equivalents of water) with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions a yellow crystalline heavy precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (*potassio-bichloride of platinum*) ($KCl, PtCl_2$). In concentrated solutions this precipitate separates immediately upon the addition of the reagent: in dilute solutions it forms only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernible under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the bichloride of platinum is added. The precipitate is difficultly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Bichloride of platinum is therefore a particularly delicate test for salts of potassa dissolved in spirit of wine. The best method of applying this reagent is to evaporate the aqueous solution of the potassa salt with bichloride of platinum nearly to dryness on the water-bath, and to pour a little water over the residue (or, better still, some spirit of wine, provided no substances insoluble in that menstruum be present), when the potassio-bichloride of platinum will be left undissolved. Care must be taken not to confound this double salt with ammonio-bichloride of platinum, which greatly resembles it (see § 91, 4).

4. *Tartaric acid* produces in neutral or alkaline* solutions—a white, quickly subsiding, *granular* crystalline precipitate of ACID TARTRATE OF POTASSA ($KO, HO, C_8H_4O_{10}$). In concentrated solutions this precipitate separates immediately; in dilute solutions often only after the lapse of a *considerable* time. Vigorous shaking or stirring of the fluid greatly promotes its formation. Very dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate; it is sparingly soluble in cold, but pretty readily soluble in hot water. In acid solutions the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda.

*Acid tartrate of soda* answers still better as a test for potassa than free tartaric acid. The reaction is the same in kind, but different in degree, being much more delicate with the salt than with the free acid, since where the former is used the soda salt of the acid combined with the

* *To alkaline solutions* the reagent must be added until the fluid shows a strongly *acid reaction.*

potassa is formed, whereas where free tartaric acid is the test applied the hydrate of the acid combined with the potassa is formed, which tends to increase the dissolving action of the water present upon the acid tartrate of potassa, and thus to check the separation of the latter ($KO, NO_5 + NaO, HO, C_8H_4O_{10} = KO, HO, C_8H_4O_{10} + NaO, NO_5$).

5. If a potassa salt which is volatile at an intense red heat is held on the loop of a fine platinum wire in the fusing zone of the Bunsen *gas-lamp* (p. 23), the salt volatilizes, and imparts a BLUE VIOLET tint to the part of the flame above the sample. Chloride of potassium and nitrate of potassa volatilize rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly; but they all of them distinctly show the reaction, though decreasing in degree. If it is wished to obtain a more uniform manifestation of the reaction, *i.e.* a manifestation independent of the nature of the acid that may chance to be combined with the potassa, the sample need simply be moistened with sulphuric acid, dried at the border of the flame, and then introduced into the fusing zone. With silicates, and other compounds of potassa of difficult volatility, the reaction may be ensured by fusing the sample first with pure gypsum, as this serves to form silicate of lime and sulphate of potassa, which latter salt then readily colors the flame. Decrepitating salts are ignited in a platinum spoon before they are attached to the loop. The sample of the potassa salt may also be held before the apex of the inner *blowpipe flame* produced with a spirit-lamp. Presence of a salt of soda completely obscures the potassa coloration of the flame.

The spectrum of the potassa flame produced by the *spectroscope* (p. 28, or p. 29) is shown on Table I. It contains two characteristic lines, the red line $\alpha$ and the indigo blue line $\beta$. If the potassa flame is observed through the *indigo prism* (p. 27) the coloration appears sky-blue, violet, and at last intensely crimson, even through the thickest layers of the solution. Admixtures of lime, soda, and lithia compounds do not alter this reaction, as the yellow rays cannot penetrate the indigo solution, and the rays of the lithia flame also are only able to pass through the thinner layers of that solution, but not through the thicker layers; the exact spot where the penetrating power of the rays of the lithia flame ceases has to be marked by the operator on his indigo prism. But organic substances which impart luminosity to the flame might lead to mistakes, and must therefore, if present, first be removed by combustion. Instead of the indigo prism a blue glass may be used; if lithia is present the glass must be sufficiently thick to keep out the red lithia rays.

6. If a salt of potassa (chloride of potassium answers best) is heated with a small quantity of water, *alcohol* (burning with colorless flame) added, heated, and then kindled, the flame appears VIOLET. The presence of soda obscures this reaction, which is altogether much less delicate than the one described in 5.

## § 90.

### *b.* SODA (NaO).

1. SODA and its HYDRATE and SALTS present in general the same properties *and reactions as potassa* and its corresponding compounds. *The oily fluid which soda forms by* deliquescing in the air resolidifies

speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily; the crystals ($NaO,CO_2 + 10$ aq.) effloresce rapidly when exposed to the air. The same applies to the crystals of sulphate of soda ($NaO,SO_3 + 10$ aq.)

2. If a sufficiently concentrated solution of a soda salt with neutral or alkaline reaction is mixed, for greater convenience, in a watch-glass, with a solution of granular *antimonate of potassa* prepared according to the directions of § 51, the mixture remains clear at first, or appears only slightly turbid; but upon rubbing the part of the glass wetted by the fluid with a glass rod, a crystalline precipitate of ANTIMONATE OF SODA ($NaO,SbO_5 + 7$ aq.) speedily separates, which makes its appearance first along the lines rubbed with the rod, and subsides from the fluid as a heavy sandy precipitate. From dilute solutions of soda salts the precipitate separates only after some time, occasionally as much as twelve hours. From very dilute solutions it does not separate at all. The precipitated antimonate of soda is *invariably* crystalline. Where it has separated slowly it occasionally consists of well-formed microscopic cubic octahedrons, but more frequently of four-sided columns tapering pyramid fashion; where it has separated promptly, it appears in the form of small boat-shaped crystals. Presence of large quantities of salts of potassa interferes very considerably with the reaction. Acid solutions cannot be tested with antimonate of potassa, as free acids will separate from the latter substance hydrated antimonic acid or acid antimonate of potassa. It is indispensable therefore, before adding the reagent, to remove, if possible, the free acid by evaporation or ignition, or where this is not practicable, by neutralizing the acid solution with a little carbonate of potassa until the reaction is feebly alkaline. It should also be borne in mind that only such solutions can be tested with antimonate of potassa which contain no other bases besides soda and potassa.

3. If salts of soda are held in the fusing zone of the Bunsen *gas-lamp*, or in the inner *spirit blowpipe flame*, they show, with regard to their relative volatility and the action of decomposing agents upon them, a similar deportment to the salts of potassa; the soda salts are, however, a little less volatile than the corresponding potassa salts. But the most characteristic sign of the presence of soda salts is the INTENSE YELLOW COLORATION which they impart to the flame. This reaction will effect the detection of even the minutest quantities of soda, and is not obscured even by the presence of large quantities of potassa.

The spectrum (Table I.) shows only a single yellow line $\alpha$ in an ordinary *spectroscope*, but with a very powerful apparatus two lines will be visible distinctly, although they are exceedingly close to each other. The reaction is so delicate that the chloride of sodium contained in atmospheric dust generally suffices to give a soda spectrum, although a faint one.

It is characteristic of the soda flame that a crystal of bichromate of potassa appears colorless in its light, and that a slip of paper coated with iodide of mercury appears white with a faint shade of yellow (BUNSEN); also that it looks orange yellow when observed through a *green glass* (MERZ). These reactions are not obscured by presence of salts of potassa, lithia, and lime.

4. If salts of soda (chloride of sodium answers best) are treated as *stated p. 83, 6, the alcohol flame* is colored intensely YELLOW. The *presence of a potassa* salt does not impair the distinctness of this reaction.

5. *Bichloride of platinum* produces no precipitate in neutral or acid solutions of soda salts. Sodio-bichloride of platinum dissolves readily both in water and in spirit of wine; it crystallizes in rosy prisms.

6. *Tartaric acid* and *acid tartrate of soda* fail to precipitate even concentrated neutral solutions of soda salts.

## § 91.

### c. AMMONIA ($NH_4O$).

1. Anhydrous AMMONIA ($NH_3$) is gaseous at the common temperature; but we have most frequently to deal with it in its aqueous solution, in which it betrays its presence at once by its penetrating odor. It is expelled from this solution by the application of heat. It may be assumed that the solution contains it as oxide of ammonium ($NH_4O$) (see § 35).

2. All the SALTS OF AMMONIA are volatile at a low heat, either with or without decomposition. Most of them are readily soluble in water. The solutions are colorless. The neutral compounds of ammonia with strong acids do not alter vegetable colors.

3. If salts of ammonia are triturated together with *hydrate of lime*, best with the addition of a few drops of water, or are, either in the solid state or in solution, heated with solution of *potassa* or of *soda*, the ammonia is liberated in the gaseous state, and betrays its presence—1, by its characteristic ODOR; 2, by its REACTION on moistened test-papers; and 3, by giving rise to the formation of WHITE FUMES when any object (*e.g.* a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes arise from the formation of solid ammoniacal salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of a mistake. If the expulsion of the ammonia is effected in a small beaker, best with hydrate of lime, with addition of a very little water, and the beaker is covered with a watch-glass having a slip of moistened turmeric or reddened litmus paper attached to the centre of the convex side, the reaction will show the presence of even very minute quantities of ammonia; only it is not immediate in such cases, but requires some time for its manifestation. It is promoted and accelerated by application of a gentle heat.

4. *Bichloride of platinum* shows the same deportment with salts of ammonia as with salts of potassa; the yellow precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM ($NH_4Cl,PtCl_2$) consists, like the corresponding potassium compound, of octahedrons discernible under the microscope.

5. *Tartaric acid* throws down after some time from most highly concentrated solutions with neutral reaction part of the ammonia as ACID TARTRATE OF AMMONIA ($NH_4O,HO,C_8H_4O_{10}$). Less concentrated solutions are not precipitated. *Acid tartrate of soda* precipitates concentrated solutions more completely, and produces a precipitate even in more dilute solutions. The precipitate is white and crystalline. Its separation may be promoted by shaking the glass, or rubbing it inside with a glass rod. By solvents it is acted upon like the corresponding *potassa salt, only that it is a little* more readily soluble in water and *in acids.*

§ 92.

*Recapitulation and remarks.*—The salts of potassa and soda are not volatile at a moderate red heat, whilst the salts of ammonia volatilize readily; the latter may therefore be easily separated from the former by ignition. The expulsion of *ammonia* from its compounds by hydrate of lime affords the surest means of ascertaining the presence of this substance. Salts of potassa can be detected in the wet way only after the removal of the ammoniacal salts which may be present, since both classes of salts manifest the same or a similar deportment with bichloride of platinum and tartaric acid. After the removal of the ammonia the *potassa* is clearly and positively characterized by either of these two reagents. Let it be borne in mind always that the reactions will only show in concentrated fluids, and that dilute solutions must therefore first be concentrated. A single drop of a *concentrated* solution will give a positive result, which cannot be obtained with a large quantity of a dilute fluid. The most simple way of detecting the potassa in the two sparingly soluble compounds that have come under our consideration here—viz., the potassio-bichloride of platinum and the acid tartrate of potassa—is to decompose these salts by gentle ignition; the former thereupon yields the potassa in the form of chloride of potassium, the latter in the form of carbonate of potassa. For the direct detection of potassium in iodide of potassium tartaric acid is better suited than bichloride of platinum, since where the latter reagent is used the separation of the platino-chloride of potassium is interfered with in consequence of the formation of a dark red fluid containing biniodide and iodide of platinum and free iodine. As regards *soda*, this alkali may be detected with positive certainty in the wet way by antimonate of potassa, provided the reagent be properly prepared and freshly dissolved, and the soda salt solution be concentrated, neutral, or feebly alkaline, and free from other bases, and that it be borne in mind that antimonate of soda invariably separates in the crystalline form, and never in a flocculent state. To detect in this way very minute quantities of soda in presence of a large proportion of potassa, precipitate the latter alkali first with bichloride of platinum, filter, remove the platinum from the filtrate by hydrosulphuric acid (§ 127), filter, evaporate the filtrate to dryness, ignite gently, dissolve the residue in a very little water, and then test the solution finally with antimonate of potassa.

Potassa and soda may be detected much more readily and speedily than in the wet way, and also with far greater delicacy, by the flame coloration. We have seen, indeed, that the soda coloration completely obscures the potassa coloration, even though the potassa salt contains only a trifling admixture of soda salt. But with the aid of the spectrum apparatus the spectra of the two are obtained so distinct and beautiful that a mistake is altogether impossible. And even without a spectrum apparatus the potassa coloration can always be distinctly recognised through the indigo prism, or through a blue glass, even in a flame colored strongly yellow by soda; and the soda coloration again may be placed beyond doubt, if necessary, with the aid of iodide of mercury paper, or green glass, in the manner already described.

The following methods serve for the detection of *ammonia in exceedingly minute quantities*, as for instance in natural waters; they depend upon the separation of certain mercury compounds which are insoluble

in water, and which contain the nitrogen or the nitrogen and part of the hydrogen of the ammonia.

*a.* If water containing a trace of ammonia or carbonate of ammonia is mixed with a few drops of solution of chloride of mercury, a white precipitate is formed, even in very dilute solution; the precipitate consists of $NH_2Hg_2Cl$, and may be considered as a double amide and chloride of mercury or as chloride of dimercurammonium: $2NH_3 + 2HgCl = NH_2Hg_2Cl + NH_4Cl$. If the solution is extraordinarily dilute no turbidity occurs, but on the addition of a few drops of solution of carbonate of potassa or carbonate of soda, the fluid will become turbid or opalescent after a few minutes. This reaction takes place when water containing a trace of a neutral salt of ammonia is mixed with a few drops of solution of chloride of mercury and a few drops of solution of carbonate of potassa or carbonate of soda. The precipitate which separates on the addition of carbonate of soda consists of one equivalent of the previously mentioned precipitate with two equivalents of oxide of mercury: $NH_3 + 4HgCl + 3KO,CO_2 = (NH_2Hg_2Cl + 2HgO) + HO + 3KCl + 3CO_2$. Too much chloride of mercury and carbonate of soda must not be added, otherwise a yellow precipitate of oxychloride of mercury would be formed. (Bohlig, Schöyen.)

*b.* Upon adding to a solution of iodide of mercury and potassium containing potassa* a little of a fluid containing ammonia, or an ammonia salt, a reddish-brown precipitate is formed if the ammonia is present in some quantity; but there is, at any rate, always a yellow coloration produced, even if only *most minute* traces of ammonia are present. The precipitate consists of tetramercurammonium iodide ($NHg_4I,2HO$): $4(HgI,KI) + 3KO + NH_3 = (NHg_4I + 2HO) + 7KI + HO$. Application of heat promotes the separation of the precipitate. Presence of chlorides of the alkali metals, or of salts of the alkalies with oxygen acid, does not interfere with the reaction; but presence of cyanide of potassium, and of sulphide of potassium, will prevent it (J. Nessler).

## § 93.

### *Special Reactions of the rarer Oxides of the first group.*

#### 1. Oxide of Cæsium (CsO), and 2. Oxide of Rubidium (RbO).

The cæsium and rubidium compounds are, it would appear, found pretty widely disseminated in nature, but in very minute quantities only. They have hitherto been found chiefly in the mother liquors of mineral waters, and in a few minerals (lepidolite, melaphyr, carnallite). Cæsium has been found in considerable quantities in pollux, and traces of rubidium have been found in the ashes of plants. The cæsium and rubidium compounds bear in general great resemblance to the potassium compounds, more particularly in this, that their concentrated aqueous solutions are precipitated by *tartaric acid* and by *bichloride of platinum*, and also that those of them that are volatile at a red heat tinge the *flame* violet. The most notable characteristic differences, on the other hand, are that the precipitates produced by bichloride of platinum are far more insoluble in water than the potassio-bichloride of platinum; 100 grm. water will, at 10° dissolve 900 mgrm. potassio-bichloride of platinum; but only 154 mgrm. of the rubidio-bichloride of platinum, and as little as 50 mgrm. of the cæsio-

* Prepared as follows. Dissolve 2 grm. iodide of potassium in 5 c.c. water, heat the solution, and add iodide of mercury till the last portion remains undissolved. Let the mixture cool, *then dilute with 20 c.c.* water. Let the fluid stand some time, *filter, and mix 20 c.c. of the filtrate with 30* c.c. of a concentrated solution of potassa. *should the fluid turn turbid, filter it* once more.

bichloride of platinum. Again, the alums show great differences as regards their solubility in cold water; thus 100 parts of water at 17° dissolve 13·5 parts of potassium alum, 2·27 parts of rubidium alum, and ·619 parts of cæsium alum. But above all, the flames colored by cæsium and rubidium compounds give *spectra* quite different from the potassium spectrum (see Table I.). The cæsium spectrum is especially characterized by the two blue lines $\alpha$ and $\beta$, which are remarkable for their wonderful intensity and sharp outline; also by the line $\gamma$, which, however, is less strongly marked. Amongst the lines in the rubidium spectrum, the splendid indigo-blue lines marked $\alpha$ and $\beta$ strike the eye by their extreme brilliancy. Less brilliant, but still very characteristic, are the lines $\delta$ and $\gamma$. To detect both alkalies in presence of each other by the spectroscope, the chlorides should be taken and not the carbonates, since with the latter salts the rubidium spectrum is not always distinct in the presence of the cæsium spectrum (ALLEN, HEINTZ). Lastly, we have still to mention that carbonate of oxide of cæsium is soluble in absolute alcohol, whilst carbonate of oxide of rubidium is insoluble in that menstruum. Still, a separation of the two oxides is effected only with difficulty by this means, as they seem to form a double salt which is not absolutely insoluble in alcohol. It is more easy to separate them when they are in the form of acid tartrates; the acid tartrate of rubidium dissolves in 8·5 parts of boiling water, and 84·57 parts of water at 25°, while the corresponding salt of cæsium dissolves in 1·02 parts of boiling water, and 10·32 parts of water at 25° (ALLEN). (The acid tartrate of potassa requires 15 parts of boiling water, and 89 parts of water at 25°.)

### 3. LITHIA (Li O).

Lithia is also found pretty widely disseminated in nature, but in minute quantities only. It is often met with in the analysis of mineral waters and ashes of plants, less frequently in the analysis of minerals, and only rarely in that of technical and pharmaceutical products. Lithia forms the transition from the first to the second group. It dissolves with difficulty in water; it does not attract moisture from the air. Most of its salts are soluble in water; some of them are deliquescent (chloride of lithium). Carbonate of lithia is difficultly soluble, particularly in cold water. *Phosphate of soda* produces in not over-dilute solutions of salts of lithia upon boiling, a white crystalline precipitate of tribasic phosphate of lithia ($3\,Li\,O,P\,O_5 + aq.$) which quickly subsides to the bottom of the precipitating vessel. This reaction, which is characteristic of lithia, is rendered much more delicate by adding with the phosphate of soda a little solution of soda, just sufficient to leave the reaction alkaline, evaporating the mixture to dryness, treating the residue with water, and adding an equal volume of liquid ammonia. By this course of proceeding even very minute quantities of lithia will be separated as $3\,Li\,O,P\,O_5 + aq.$ The precipitate fuses before the blowpipe, and gives upon fusion with carbonate of soda a clear bead; when fused upon charcoal it is absorbed by the pores of the latter body. It dissolves in hydrochloric acid to a fluid which, when diluted and supersaturated with ammonia, remains clear in the cold, but upon boiling gives a heavy crystalline precipitate of $3\,Li\,O,P\,O_5 + aq.$ (Reactions by which the phosphate of lithia differs from the phosphates of the alkaline earths). *Tartaric acid* and *bichloride of platinum* fail to precipitate even concentrated solutions of salts of lithia. If salts of lithia are exposed to the *gas* or *blowpipe-flame*, in the manner described § 89, 5, they tinge the flames carmine-red. Silicates containing lithia demand addition of gypsum to produce this reaction. Phosphate of lithia will tinge the flame carmine-red if the fused bead is moistened with hydrochloric acid. The soda coloration conceals the lithia coloration; in presence of soda, therefore, the lithia tint must be viewed through a blue glass, or through a thin layer of indigo solution. Presence of a small proportion of potassa will not conceal the lithia coloration. In presence of a large proportion of potassa, the lithia may be identified by placing the substance in the fusing zone, viewing the colored flame through the indigo prism and comparing it with a pure potassa flame produced in the opposite part of the fusing zone. Viewed through thin layers, the lithia-colored flame appears now redder than the pure potassa flame; viewed through somewhat thicker layers, the flames appear at last equally red, if the proportion of the lithia to the potassa is only trifling; but when lithia predominates in the examined sample the intensity of the red coloration imparted by lithia decreases perceptibly when viewed through thicker layers, whilst the pure potassa-flame is scarcely impaired thereby. By this means lithia may be detected in potassa salts, even though present only in the proportion of one part in several thousand parts of the latter. Soda, unless present in over-large quantities, interferes but little with these reactions (CARTMELL, BUNSEN).

*The lithium spectrum* (Tab. I.) is most brilliantly characterized by the splendid *carmine-red line a*, and the orange-yellow very faint line β. The flame of a Bunsen

burner yields only these two lines, but if chloride of lithium is introduced into a hydrogen flame, a dull blue line is perceptible which becomes brilliant if the oxyhydrogen flame is used. Its position almost coincides with the weaker of the two blue lines of cæsium (TYNDALL, FRANKLAND). If alcohol be poured over chloride of lithium, and then ignited, the flame shows also a carmine-red tint. Presence of salts of soda will mask this reaction.

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To detect small quantities of cæsium, rubidium, and lithium in presence of very large quantities of soda or potassa, extract the dry chlorides, with addition of a few drops of hydrochloric acid, with alcohol of 90 per cent., which leaves behind the far larger portion of the chloride of sodium and chloride of potassium. Evaporate the solution to dryness, dissolve the residue in a little water, and precipitate with bichloride of platinum. Filter the fluid off, boil the precipitate repeatedly with small quantities of water, to remove the potassio-bichloride of platinum present, and examine in the course of this process repeatedly by the spectroscope. The potassa spectrum will now be found to grow fainter and fainter, whilst the spectra of rubidium and cæsium will become visible, if these metals are present. Evaporate the fluid filtered off from the platinum precipitate to dryness, heat the residue to slight redness in the hydrogen current, to decompose the sodio-bichloride of platinum and the excess of bichloride of platinum, moisten with hydrochloric acid, drive off the acid again, and extract the chloride of lithium finally with a mixture of absolute alcohol and ether. The evaporation of the solution obtained leaves the chloride of lithium behind in a state of almost perfect purity; it may then be further examined and tested. Before drawing from the simple coloration of the flame the conclusion that lithia is present, it is advisable, in order to guard against the chance of error, to test a portion of the residue, dissolved in water, with sulphuric acid and alcohol, to make quite sure that strontia or lime is not present. The addition of hydrochloric acid, which is repeatedly prescribed in the above process to precede the extraction of the chloride of lithium with alcohol, is necessary for this reason, that chloride of lithium is, even at a moderate red heat, converted by the action of aqueous vapour into caustic lithia, which then attracts carbonic acid, forming carbonate of lithia, which is insoluble in alcohol.

## § 94.

### SECOND GROUP.

### BARYTA, STRONTIA, LIME, MAGNESIA.

*Properties of the group.*—The alkaline earths are soluble in water in the pure (caustic) state. Magnesia, however, dissolves but very sparingly in water. The solutions manifest alkaline reaction; the alkaline reaction of magnesia is most clearly apparent when that earth is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of the salts of the alkaline earths are therefore precipitated by carbonates and phosphates of the alkalies. This reaction distinguishes the oxides of the second group from those of the first. From the oxides of the other groups they are distinguished by the solutions being neither precipitated by hydrosulphuric acid, nor by sulphide of ammonium. The alkaline earths and their salts are white or colorless, and not volatile at a moderate red heat. The solutions of their nitrates and chlorides are not precipitated by carbonate of baryta.

*Special Reactions.*

## § 95.

### *a.* BARYTA (Ba O).

1. BARYTA *is pretty readily soluble in hot water, but rather sparingly so in cold water; it dissolves freely in dilute hydrochloric or*

nitric acid. Hydrate of baryta fuses at a red heat, without losing its water.

2. Most of the SALTS OF BARYTA are insoluble in water. The soluble salts do not affect vegetable colours, and are decomposed upon ignition in a glass tube, with the exception of chloride, bromide, and iodide of barium. The insoluble salts dissolve in dilute hydrochloric acid, except the sulphate of baryta and the silico-fluoride of barium. Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air. Concentrated solutions of baryta are precipitated by hydrochloric or nitric acid added in large proportions, as chloride of barium and nitrate of baryta are not soluble in the aqueous solutions of the said acids.

3. *Ammonia* produces no precipitate in aqueous solutions of salts of baryta; *potassa* or *soda* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTA ($BaO, HO + 8$ aq.) produced by potassa or soda.

4. *Carbonates of the alkalies* throw down CARBONATE OF BARYTA ($BaO, CO_2$) in the form of a white precipitate. If the solution was previously acid, complete precipitation takes place only upon heating the fluid. In chloride of ammonium the precipitate is soluble to a trifling yet clearly perceptible extent; carbonate of ammonia therefore produces no precipitate in very dilute solutions of baryta containing much chloride of ammonium.

5. *Sulphuric acid* and all the soluble *sulphates*, more particularly also solution of *sulphate of lime*, produce even in very dilute solutions, a heavy, finely pulverulent, white precipitate of SULPHATE OF BARYTA ($BaO, SO_3$), which is insoluble in alkalies, nearly so in dilute acids, but perceptibly soluble in boiling concentrated hydrochloric and nitric acids, as well as in concentrated solutions of ammonia salts; however, in these latter only if there is no excess of sulphuric acid or a sulphate present. This precipitate is generally formed immediately upon the addition of the reagent; from highly dilute solutions, however, especially when strongly acid, it separates only after some time.

6. *Hydrofluosilicic acid* throws down SILICO-FLUORIDE OF BARIUM ($BaF, SiF_2$) in the form of a colorless crystalline quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is perceptibly soluble in hydrochloric and nitric acids. Addition of an equal volume of alcohol hastens the precipitation and makes it so complete that the filtrate remains clear upon addition of sulphuric acid.

7. *Phosphate of soda* produces in neutral or alkaline solutions a white precipitate of PHOSPHATE OF BARYTA ($2\,BaO, HO, PO_5$) which is soluble in free acids. Addition of ammonia only slightly increases the quantity of this precipitate, a portion of which is in this process converted into basic phosphate of baryta ($3\,BaO, PO_5$). Chloride of ammonium dissolves the precipitate to a clearly perceptible extent.

8. *Oxalate of ammonia* produces in moderately dilute solutions a white pulverulent precipitate of OXALATE OF BARYTA ($2\,BaO, C_2O_3 + 2$ aq.), which is soluble in hydrochloric and nitric acids. When recently thrown down, this precipitate dissolves also in oxalic and acetic acids; but the *solutions speedily* deposit binoxalate of baryta ($BaO, HO, C_2O_3 + 2$ aq.) *in the form of* a crystalline powder.

9. *Chromate of potassa*, and bichromate of potassa, produce a bright yellow precipitate of chromate of baryta ($BaO, CrO_3$) even in very dilute solutions of salts of baryta. The precipitate dissolves readily in hydrochloric or nitric acid to a yellowish red solution, from which it is thrown down again by ammonia.

10. If soluble salts of baryta in powder are heated with dilute *spirit of wine*, they impart to the flame a GREENISH-YELLOW color.

11. If salts of baryta are held on the loop of a platinum wire in the fusing zone of the Bunsen *gas flame*, the part of the flame above the sample is colored YELLOWISH GREEN; or if the baryta salts are held in the inner spirit *blowpipe flame*, the same coloration is imparted to the part of the flame before the sample. With the soluble baryta salts, and also with the carbonate and sulphate of baryta, the reaction is immediate or very soon; but the phosphate demands previous moistening of the sample with sulphuric acid or hydrochloric acid, by which means the baryta may be detected by the flame coloration also in silicates decomposable by acids. Silicates which hydrochloric acid fails to decompose must be fused with carbonate of soda, when the carbonate of baryta produced will show the reaction. It is characteristic of the yellowish-green baryta coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are selected for the experiment, presence of lime and strontia will not interfere with the reaction. The baryta *spectrum* is shown in Table I. The green lines, $\alpha$ and $\beta$ are the most intense; $\gamma$ is less marked, but still characteristic. The platinum wire sometimes contains barium (KRAUT), hence it is well to see first whether it will give a barium spectrum by itself.

12. Cold solutions of *bicarbonates of the alkalies* or of *carbonate of ammonia* fail to decompose sulphate of baryta, or, to speak more correctly, they decompose that salt only to a scarcely perceptible extent; the same applies to a boiling solution of 1 *part of carbonate and* 3 *parts of sulphate of potassa*. Repeated action of boiling solutions of simple or monocarbonates of the alkalies upon sulphate of baryta succeeds in the end completely in decomposing that salt. It is readily decomposed also by fusion with carbonates of the alkalies, which results in the formation of a sulphate of the alkali, soluble in water, and of carbonate of baryta, insoluble in that menstruum.

## § 96.

### *b.* STRONTIA (SrO).

1. STRONTIA and its HYDRATE and SALTS have nearly the same general properties and reactions as baryta and its corresponding compounds. Hydrate of strontia is more sparingly soluble in water than hydrate of baryta. Chloride of strontium dissolves in absolute alcohol and deliquesces in moist air. Nitrate of strontia is insoluble in absolute alcohol and does not deliquesce in the air.

2. The salts of strontia show with *ammonia*, *potassa*, and *soda*, and also with the *carbonates of the alkalies* and with *phosphate of soda*, nearly the same reactions as the salts of baryta. Carbonate of strontia dissolves *somewhat more difficultly* in chloride of ammonium than *carbonate of baryta*.

3. *Sulphuric acid* and *sulphates* throw down SULPHATE OF STRONTIA ($SrO, SO_3$) in the form of a white precipitate. Thrown down by dilute sulphuric acid from concentrated solutions, it is at first flocculent and amorphous, afterwards pulverulent and crystalline: thrown down by dilute sulphuric acid from dilute solutions, or produced by solutions of sulphates, it is immediately pulverulent and crystalline. Application of heat greatly promotes the precipitation. Sulphate of strontia is far more soluble in water than sulphate of baryta: owing to this readier solubility, the precipitated sulphate of strontia separates from rather dilute solutions only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if solution of *sulphate of lime* is used as precipitant. Sulphate of strontia is insoluble in spirit of wine; addition of alcohol will therefore promote the separation of the precipitate. In hydrochloric acid and in nitric acid sulphate of strontia dissolves perceptibly. Presence of large quantities of these acids will accordingly most seriously impair the delicacy of the reaction. Solution of sulphate of strontia in hydrochloric acid is, after dilution with water, rendered turbid by chloride of barium. Sulphate of strontia does not dissolve on boiling in a concentrated solution of sulphate of ammonia.

4. *Hydrofluosilicic acid* fails to produce a precipitate even in concentrated solutions; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

5. *Oxalate of ammonia* precipitates even from rather dilute solutions OXALATE OF STRONTIA ($2\,SrO, C_2O_3 + 5\,aq.$) in the form of a white powder, which dissolves readily in hydrochloric and nitric acid, and perceptibly in salts of ammonia, but is only sparingly soluble in oxalic and acetic acid.

6. *Bichromate of potassa* does not precipitate solutions of salts of strontia, even when they are concentrated. *Neutral chromate of potassa* at first produces no precipitate, but on long standing, if the solution is not very dilute, light yellow chromate of strontia separates in the crystalline form. The crystals are but slightly soluble in water, but readily soluble in hydrochloric, nitric, and chromic acids.

7. If salts of strontia soluble in water or alcohol are heated with dilute spirit of wine, and the spirit is kindled, the flame appears of a very intense CARMINE color, more particularly upon stirring the alcoholic mixture.

8. If a strontia salt is held in the fusing zone of the Bunsen *gas flame*, or in the inner spirit *blowpipe flame*, an INTENSELY RED color is imparted to the flame. With chloride of strontium the reaction is the most distinct, less clear with strontia and carbonate of strontia, fainter still with sulphate of strontia, and scarcely at all with strontia salts of fixed acids. The sample is therefore, after its first exposure to the flame, moistened with hydrochloric acid, and then again exposed to the flame. If sulphate of strontia is likely to be present, the sample is first exposed a short time to the reducing flame (to produce sulphide of strontium), before it is moistened with hydrochloric acid. Viewed through the *blue glass*, the strontia flame appears purple or rose (difference between strontia and lime, which latter body shows a faint greenish grey color when treated in this manner); this reaction is the *most clearly apparent* if the sample moistened with hydrochloric acid is *let spirt up in the* flame. In presence of baryta the strontia reaction

shows only upon the first introduction of the sample moistened with hydrochloric acid into the flame. The strontia *spectrum* is shown in Table I. It contains a number of characteristic lines, more especially the orange line $\alpha$, the red lines $\beta$ and $\gamma$, and the blue line $\delta$, which latter is more particularly suited for the detection of strontia in presence of baryta and lime.

9. Sulphate of strontia is completely decomposed by continued digestion with solutions of *carbonate of ammonia* or of *bicarbonates of the alkalies*, but much more rapidly by boiling with a solution of 1 part of *carbonate of potassa and* 3 *parts of sulphate of potassa* (essential difference between sulphate of strontia and sulphate of baryta).

## § 97.

### *c.* LIME (Ca O).

1. LIME and its HYDRATE and SALTS present in their general properties and reactions, a great similarity to baryta and strontia and their corresponding compounds. Hydrate of lime is far more difficultly soluble in water than the hydrates of baryta and strontia; it dissolves also more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol and deliquesce in the air.

2. *Ammonia, potassa, carbonates of the alkalies* and *phosphate of soda* show nearly the same reactions with salts of lime as with salts of baryta. Recently precipitated CARBONATE OF LIME ($Ca O, C O_2$) is bulky and amorphous—after a time, and immediately upon application of heat, it falls down and assumes a crystalline form. Recently precipitated carbonate of lime dissolves pretty readily in solution of chloride of ammonium; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in form of crystals.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in highly concentrated solutions white precipitates of SULPHATE OF LIME ($Ca O, S O_3, H O$ + aq.), which redissolve completely in a large proportion of water, and are still far more soluble in acids. Sulphate of lime dissolves readily on boiling in a concentrated solution of sulphate of ammonia. In less concentrated solutions of lime the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solution of sulphate of lime of course cannot produce a precipitate in salts of lime; but even a cold saturated solution of sulphate of potassa, mixed with 3 parts of water, produces a precipitate only after standing from twelve to twenty-four hours. In solutions of lime which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will form upon addition of two volumes of alcohol either immediately, or after the lapse of some time.

4. *Hydrofluosilicic acid* does not precipitate salts of lime, even when an equal volume of alcohol is added.

5. *Oxalate of ammonia* produces a white pulverulent precipitate of OXALATE OF LIME. If the fluids are in any degree concentrated or hot, the precipitate ($2 Ca O, C_4O_6$ + 2 aq.) forms at once; but if they are very dilute and cold, it forms only after some time, in which latter case it is more distinctly crystalline and consists of a mixture of the above salt *with* $2 Ca O, C_4O_6 + 6$ *aq.* Oxalate of lime dissolves readily in hydro-

chloric and nitric acids; but acetic and oxalic acids fail to dissolve it to any perceptible extent.

6. Neither *chromate of potassa* nor bichromate of potassa precipitate solutions of salts of lime.

7. Soluble salts of lime when heated with dilute *spirit of wine* impart to the flame of the latter a YELLOWISH-RED color, which is liable to be confounded with that communicated to the flame of alcohol by salts of strontia.

8. If salts of lime are held in the fusing zone of the Bunsen *gas flame*, or in the inner spirit *blowpipe flame*, they impart to the flame a YELLOWISH-RED color. This reaction is the most distinct with chloride of calcium; sulphate of lime shows it only after its incipient decomposition, and carbonate of lime also most distinctly after the escape of the carbonic acid. Compounds of lime with fixed acids do not color flame; those of them which are decomposed by hydrochloric acid will, however, show the reaction after moistening with that acid. The reaction is in such cases promoted by flattening the loop of the platinum wire, placing a small portion of the lime compound upon it, letting it frit, adding a drop of hydrochloric acid, which remains hanging to the loop, and then holding the latter in the fusing zone. The reaction shows now the most distinct light immediately upon the disappearance of the drop, which in this process, as in LEIDENFROST'S phenomenon, evaporates without boiling (BUNSEN). Viewed through the *green glass*, the lime coloration of the flame appears finch-green colored on letting the sample moistened with hydrochloric acid spirt in the flame (difference between lime and strontia, which latter substance under similar circumstances shows a very faint yellow. MERZ). In presence of baryta the lime reaction shows only upon the first introduction of the sample into the flame. The lime *spectrum* is shown in Table I. The intensely green line $\beta$ is more particularly characteristic, also the intensely orange line $\alpha$. It requires a very good apparatus to show the indigo-blue line to the right of $G$ in the solar spectrum, as this is much less luminous than the other lines.

9. With monocarbonates and bicarbonates of the alkalies, as also with a solution of carbonate and sulphate of potassa, sulphate of lime shows the same reactions as sulphate of strontia.

## § 98.

### *d.* MAGNESIA ($MgO$).

1. *Magnesium* is silver white, hard, ductile, of 1·74 sp. gr. It melts at a moderate red heat, and volatilizes at a white heat. When ignited in the air it burns with a dazzling white flame to magnesia. It preserves its lustre in dry air, but it gradually becomes coated with hydrate of magnesia when exposed to moist air. Pure water is not decomposed by magnesium at the ordinary temperature, but in water acidulated with hydrochloric or sulphuric acid, magnesium dissolves rapidly with evolution of hydrogen.

2. MAGNESIA and its HYDRATE are white powders of far greater bulk than the other alkaline earths and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. *Hydrate of magnesia* loses its water upon ignition.

3. Some of the SALTS OF MAGNESIA are soluble in water, others are insoluble in that fluid. The soluble salts of magnesia have a nauseous bitter taste: in the neutral state they do not alter vegetable colors; with the exception of sulphate of magnesia, they undergo decomposition when gently ignited, and the greater part of them even upon simple evaporation of their solutions. Sulphate of magnesia loses its acid at a white heat. Nearly all the salts of magnesia which are insoluble in water dissolve readily in hydrochloric acid.

4. *Ammonia* throws down from the solutions of neutral salts part of the magnesia as HYDRATE ($MgO, HO$) in the form of a white bulky precipitate. The rest of the magnesia remains in solution as a double salt, VIZ., in combination with the ammonia salt which forms upon the decomposition of the salt of magnesia; these double salts are not decomposed by a small excess of ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds that ammonia fails to precipitate them in presence of a sufficient proportion of an ammonia salt with neutral reaction; or, what comes to the same, that ammonia produces no precipitate in solutions of magnesia containing a sufficient quantity of free acid, and that precipitates produced by ammonia in neutral solutions of magnesia are redissolved upon the addition of chloride of ammonium. It should be borne in mind, that in solutions containing only 1 equivalent of an ammonia salt ($NH_4O, SO_3$ or $NH_4Cl$) to 1 equivalent of magnesia salt, although no precipitate is produced by the addition of a slight excess of ammonia, a portion of the magnesia is, however, thrown down on the addition of a large excess of ammonia.

5. *Potassa*, *soda*, *baryta*, and *lime* throw down HYDRATE OF MAGNESIA. The separation of this precipitate is greatly promoted by boiling the mixture. Chloride of ammonium and other similar salts of ammonia redissolve the washed precipitated hydrate of magnesia. If the salts of ammonia are added in sufficient quantity to the solution of magnesia before the addition of the precipitant, small quantities of the latter fail altogether to produce a precipitate. However, upon boiling the solution afterwards with an excess of potassa, the precipitate will of course make its appearance, since this process causes the decomposition of the ammonia salt, removing thus the agent which retains the hydrate of magnesia in solution. It should be remembered that hydrate of magnesia is more soluble in solutions of chloride of potassium, chloride of sodium, sulphate of potassa, and sulphate of soda, than in water, and that on this account its precipitation is less complete when these salts are present in large quantities. From such solutions the magnesia is, however, thrown down, for the most part, by an excess of solution of potassa or solution of soda.

6. *Carbonate of potassa* and *carbonate of soda* produce in neutral solutions a white precipitate of BASIC CARBONATE OF MAGNESIA $4(MgO, CO_2) + MgO, HO + 10\,aq.$ One-fifth of the carbonic acid of the decomposed alkaline carbonate is liberated in the process, and combines with a portion of the carbonate of magnesia to bicarbonate, which remains in solution. This carbonic acid is expelled by boiling, and an additional precipitate formed ($MgO, CO_2 + 3\,aq.$) Application of heat therefore promotes the separation and increases the quantity of the precipitate. *Chloride of* ammonium and other similar salts of *ammonia, when present in sufficient* quantity, prevent this precipita-

tion also, and readily redissolve the precipitates after they have been washed.

7. If solutions of magnesia are mixed with *carbonate of ammonia*, the fluid always remains clear at first; but after standing some time, it deposits, more or less quickly according to the concentration of the solution, a crystalline precipitate. When the carbonate of ammonia is in slight excess, the precipitate consists of carbonate of magnesia ($MgO, CO_2 + 3$ aq.), when the carbonate of ammonia is in large excess, it consists of CARBONATE OF MAGNESIA AND AMMONIA ($NH_4O, CO_2 + MgO, CO_2 + 4$ aq.) In rather highly dilute solutions this precipitate will not form. Addition of ammonia and of excess of carbonate of ammonia promotes its separation. Chloride of ammonium counteracts it, but it cannot prevent the formation of the precipitate in rather highly concentrated solutions.

8. *Phosphate of soda* precipitates from solutions of magnesia, if they are not too dilute, PHOSPHATE OF MAGNESIA ($2MgO, HO, PO_5 + 14$ aq.) as a white powder. Upon boiling, basic phosphate of magnesia ($3MgO, PO_5 + 7$ aq.) separates, even from rather dilute solutions. But if the addition of the precipitant is preceded by that of *chloride of ammonium* and *ammonia* a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2MgO, NH_4O, PO_5 + 12$ aq.) will separate even from very dilute solutions of magnesia; its separation may be greatly promoted and accelerated by stirring with a glass rod; even should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the side of the vessel will after the lapse of some time appear distinctly as white streaks (soluble in hydrochloric acid). Water and solutions of salts of ammonia dissolve the precipitate but very slightly; but it is readily soluble in acids, even in acetic acid. In water containing ammonia it may be considered insoluble.

9. *Oxalate of ammonia* produces no precipitate in highly dilute solutions of magnesia: in less dilute solutions no precipitate is formed at first, but after standing some time crystalline crusts of various oxalates of ammonia and magnesia make their appearance. In highly concentrated solutions oxalate of ammonia very speedily produces precipitates of oxalate of magnesia ($2MgO, C_2O_3 + 4$ aq.), which contain small quantities of the above-named double salts. Chloride of ammonium, especially in presence of free ammonia, interferes with the formation of these precipitates, but will not in general absolutely prevent it.

10. *Sulphuric acid*, *hydrofluosilicic acid*, and *chromate of potassa*, do not precipitate salts of magnesia.

11. Salts of magnesia do not color flame.

## § 99.

*Recapitulation and remarks.*—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate (unless it is present in the natural form, either anhydrous or combined with 1 equivalent of water) and the disposition of salts of magnesia to form double salts with ammonia compounds, are the three principal points in which magnesia differs from the other alkaline earths. To detect magnesia in solutions *containing all the* alkaline earths, we always first remove the baryta, *strontia, and lime*. This is effected most conveniently by means of

carbonate of ammonia, with addition of some ammonia and of chloride of ammonium, and application of heat; since by this process the baryta, strontia, and lime are obtained in a form of combination suited for further examination. If the solutions are somewhat dilute, and the precipitated fluid is quickly filtered, the carbonates of baryta, strontia, and lime are obtained on the filter, whilst the whole of the magnesia is found in the filtrate. But as chloride of ammonium dissolves a little carbonate of baryta, and also a little carbonate of lime, though much less of the latter than of the former, trifling quantities of these bases are found in the filtrate; nay, where only traces of them are present, they may altogether remain in solution. In accurate experiments, therefore, the separation is effected in the following way: Divide the filtrate into three portions, test one portion with dilute sulphuric acid for the trace of baryta which it may contain in solution, and another portion with oxalate of ammonia for the minute trace of lime which may have remained in solution. If the two reagents produce no turbidity even after some time, test the third portion with phosphate of soda for MAGNESIA. But if one of the reagents causes turbidity, filter the fluid from the gradually subsiding precipitate, and test the filtrate for magnesia. Should both reagents produce precipitates, mix the two first portions together, filter after some time, and then test the filtrate. To make sure that the precipitate thrown down by oxalate of ammonia is actually oxalate of lime, and not, as it may be, oxalate of magnesia and ammonia, dissolve it in some hydrochloric acid, and add dilute sulphuric acid, and then spirit of wine.

To show the presence of the baryta, strontia, and lime in the precipitate produced by carbonate of ammonia, dissolve the precipitate in some dilute hydrochloric acid; add solution of gypsum to a small portion of this solution, when the immediate formation of a precipitate will prove the presence of BARYTA. Evaporate the remainder of the hydrochloric acid solution on the water-bath to dryness, and treat the residue with absolute alcohol, which will dissolve the chloride of strontium and the chloride of calcium, leaving the greater part of the chloride of barium undissolved. Mix the alcoholic solution with an equal volume of water and a few drops of hydrofluosilicic acid, and let the mixture stand several hours, when the last traces of the baryta present will be found precipitated as silicofluoride of barium. Filter, and add sulphuric acid to the alcoholic filtrate. This will throw down the strontia and the lime. Filter the fluid from the precipitate, wash with weak spirit of wine, and boil the sulphates for some time with a sufficient quantity of sulphate of ammonia in strong solution, renewing the water as it evaporates and adding ammonia, so as to keep the fluid slightly alkaline. Sulphate of STRONTIA remains undissolved, while the sulphate of lime dissolves. After the solution has been much diluted, the LIME may be thrown down by oxalate of ammonia. The mixture of sulphate of strontia and sulphate of lime may also be treated as follows: Boil them with solution of carbonate of soda. By this means the sulphates are converted into carbonates. Wash these, dissolve them in nitric acid, evaporate the solution to dryness, pulverize the residue and digest it for a considerable time with absolute alcohol to which a little ether has been added, when the nitrate of lime will dissolve, leaving the nitrate of strontia *undissolved. The latter* may be readily examined, by dis*solving in a small quantity of water* and adding solution of sulphate of

lime; the lime in the alcoholic solution of nitrate of lime may be detected by the addition of sulphuric acid. The precipitate of sulphate of lime thus produced, when treated with water, should yield a solution which gives an immediate and considerable precipitate with oxalate of ammonia. The best and most convenient way of detecting the alkaline earths in their phosphates, is to decompose these latter by means of sesquichloride of iron, with addition of acetate of soda (§ 142). The oxalates of the alkaline earths are converted into carbonates by ignition, preparatory to the detection of the several earths which they may contain. The following method will serve to analyse mixtures of the sulphates of the alkaline earths. Extract the mixture under examination with small portions of boiling water. The solution contains the whole of the sulphate of magnesia, unless it is present in the native anhydrous state, besides a trifling quantity of sulphate of lime. Digest the residue, according to H. ROSE's direction, in the cold for 12 hours, with a solution of carbonate of ammonia, or boil it 10 minutes with a solution of 1 part of carbonate and 3 parts of sulphate of potassa, filter, wash, then treat with dilute hydrochloric acid, which will dissolve the carbonates of strontia and lime formed, and if the anhydrous native sulphate of magnesia was present, the carbonate of magnesia or the carbonate of ammonia and magnesia, but always also a minute trace of baryta (FRESENIUS), leaving behind the undecomposed sulphate of baryta. The latter may then be decomposed by fusion with carbonates of the alkalies. The solutions obtained are to be examined further according to the above directions.

The detection of baryta, strontia, and lime in the moist way is very instructive, but also rather laborious and tedious. By means of the spectroscope these alkaline earths are much more readily detected, even when present all three together. According to the nature of the acid, the sample is either introduced at once into the flame, or after previous ignition and moistening with hydrochloric acid. To detect very minute quantities of baryta and strontia in presence of large quantities of lime, ignite a few grammes of the mixed carbonates a few minutes in a platinum crucible strongly over the blast,* extract the ignited mass by boiling with a little distilled water, evaporate with hydrochloric acid to dryness, and examine the residue by spectrum analysis (ENGELBACH).

## § 100.

### THIRD GROUP.

More common oxides:—ALUMINA, SESQUIOXIDE OF CHROMIUM.

Rarer oxides:—BERYLLA, THORIA, ZIRCONIA, YTTRIA, OXIDE OF ERBIUM, OXIDES OF CERIUM, OXIDE OF LANTHANIUM, OXIDE OF DIDYMIUM, TITANIC ACID, TANTALIC ACID, NIOBIC ACID.

*Properties of the group.*—The oxides of the third group are insoluble in water, both in the pure state and as hydrates. Their sulphides cannot be produced in the moist way. Hydrosulphuric acid therefore fails to precipitate the solutions of their salts. Sulphide of ammonium throws down, from the solutions of the salts in which the oxides of the

* The carbonates of baryta and strontia are much more readily reduced to the *caustic state in this* process than would be the case in the absence of carbonate of *lime.*

third group constitute the base,* in the same way as ammonia, the hydrated oxides. This reaction with sulphide of ammonium distinguishes the oxides of the third from those of the two preceding groups.

*Special Reactions of the more common Oxides of the third group.*

## § 101.

### *a.* ALUMINA ($Al_2O_3$).

1. ALUMINIUM is nearly white. It is not oxidized by the action of the air, in compact masses not even upon ignition. It may be filed, and is very malleable; its specific gravity is only 2·67. It is fusible at a bright red heat. It does not decompose water at a boiling heat. Aluminium dissolves readily in hydrochloric acid, as well as in hot solution of potassa, with evolution of hydrogen. Nitric acid dissolves it only slowly, even with the aid of heat.

2. ALUMINA is non-volatile and colorless; the HYDRATE is also colorless. Alumina dissolves in dilute acids slowly and with very great difficulty, but more readily in concentrated hot hydrochloric acid. In fusing bisulphate of potassa, it dissolves readily to a mass soluble in water. The hydrate in the amorphous condition is readily soluble in acids; in the crystalline state it dissolves in them with very great difficulty. After ignition with alkalies, the alumina, or, more correctly speaking, the alkaline aluminate formed, is readily dissolved by acids.

3. The SALTS OF ALUMINA are colorless and non-volatile; some of them are soluble, others insoluble. The anhydrous chloride is solid, pale yellow, crystalline, volatile. The soluble salts have a sweetish, astringent taste, redden litmus-paper, and lose their acid upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric acid are decomposed and made soluble by ignition with carbonate of soda and potassa, or bisulphate of potassa. This decomposition and solution may, however, be effected also by heating them, reduced to a fine powder, with hydrochloric acid of 25 per cent., or with a mixture of 3 parts by weight of hydrated sulphuric acid, and 1 part by weight of water, in sealed glass tubes, to 200°–210° for two hours (A. MITSCHERLICH).

4. *Potassa* and *soda* throw down from solutions of alumina salts a bulky precipitate of HYDRATE OF ALUMINA ($Al_2O_3$, 3 H O), which contains alkali and generally also an admixture of basic salt; this precipitate redissolves readily and completely in an excess of the precipitant, but from this solution it is reprecipitated by addition of chloride of ammonium, even in the cold, but more completely upon application of heat (compare § 53). The precipitate does not dissolve in excess of chloride of ammonium. The presence of salts of ammonia does not prevent the precipitation by potassa or soda.

* The oxides of the third group may nearly all of them combine to saline compounds with bases as well as with acids; alumina, for instance, combines with potassa to aluminate of potassa, with sulphuric acid to sulphate of alumina. The oxides of the third group stand, accordingly, partly on the verge between bases and acids. Those which incline *more to the latter, as is the case with the three last members of the group, are therefore also called acids.*

5. *Ammonia* also produces a precipitate of HYDRATE OF ALUMINA, which contains ammonia and an admixture of basic salt; this precipitate also redissolves in a very considerable excess of the precipitant, but with difficulty only, which is the greater the larger the quantity of salts of ammonia contained in the solution. Boiling promotes precipitation, as it drives off the excess of ammonia. It is this deportment which accounts for the complete precipitation of hydrate of alumina from solution in potassa by an excess of chloride of ammonium.

6. *Carbonates of the alkalies* precipitate BASIC CARBONATE OF ALUMINA, which is somewhat soluble in excess of fixed alkaline carbonate, and still less soluble in excess of carbonate of ammonia. Boiling promotes precipitation by the latter.

7. If the solution of a salt of alumina is digested with finely divided *carbonate of baryta*, the greater part of the acid of the alumina salt combines with the baryta, the liberated carbonic acid escapes, and the alumina precipitates completely as HYDRATE MIXED WITH BASIC SALT OF ALUMINA: even digestion in the cold suffices to produce this reaction.

N.B. to 4, 5, 6 and 7.—Tartaric, citric, and other non-volatile organic acids completely prevent the precipitation of alumina as hydrate or basic salt, when they are present in any notable quantity. The presence of sugar and similar organic substances interferes with the completeness of the precipitation.

8. *Phosphate of soda* precipitates the PHOSPHATE OF ALUMINA ($Al_2O_3, PO_5$) from solutions of salts of alumina. The bulky white precipitate is readily soluble in potash or soda solution, but not in ammonia; chloride of ammonium therefore precipitates it from its solution in potash or soda. The precipitate is readily soluble in hydrochloric or nitric acid, but not in acetic acid (difference from alumina); acetate of soda, therefore, precipitates it from its solution in hydrochloric acid, if the latter is not too predominant. Tartaric acid, sugar, &c., do not prevent the precipitation of phosphate of alumina, but citric acid does prevent it (ROSE).

9. *Oxalic acid* and its salts do not precipitate the solutions of salts of alumina.

10. *Sulphate of potash*, added to very concentrated solutions of salts of alumina, occasions the gradual separation in the form of crystals, or a crystalline powder of sulphate of alumina and potash ($KO,SO_3 + Al_2O_3,3SO_3 + 24$ aq.)

11. If alumina or one of its compounds is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of *nitrate of protoxide of cobalt*, and then again strongly ignited, an unfused mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candlelight it appears violet. This reaction is in a measure to be relied on only in the case of infusible or difficultly fusible compounds of alumina pretty free from other oxides; it is never quite decisive, since cobalt solution gives a blue color under similar circumstances not only with readily fusible compounds, but also with certain infusible compounds free from alumina, such as the neutral phosphates of the alkaline earths.

## § 102.

### *b.* SESQUIOXIDE OF CHROMIUM ($Cr_2O_3$).

1. SESQUIOXIDE OF CHROMIUM is a green, its HYDRATE a bluish gray-green powder. The hydrate dissolves readily in acids; the non-ignited sesquioxide dissolves more difficultly, and the ignited sesquioxide is almost altogether insoluble.

2. The SALTS OF SESQUIOXIDE OF CHROMIUM have a green or violet color. Many of them are soluble in water. Most of them dissolve in hydrochloric acid. The solutions exhibit a fine green or a dark violet color, which latter, however, changes to green upon heating. The salts of sesquioxide of chromium with volatile acids are decomposed upon ignition, the acids being expelled. The salts of sesquioxide of chromium which are soluble in water redden litmus. Anhydrous sesquichloride of chromium is crystalline, violet-colored, insoluble in water and in acids, and volatilizes with difficulty.

3. *Potassa and soda* produce in the green as well as in the violet solutions a bluish-green precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM, which dissolves readily and completely in an excess of the precipitant, imparting to the fluid an emerald-green tint. Upon *long-continued* ebullition of this solution, the whole of the hydrated sesquioxide separates again, and the supernatant fluid appears perfectly colorless. The same reprecipitation takes place if chloride of ammonium is added to the alkaline solution. Application of heat promotes the separation of the precipitate.

4. *Ammonia* produces in green solutions a grayish-green, in violet solutions a grayish-blue precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM. The former precipitate dissolves in acids to a green fluid, the latter to a violet fluid. Other circumstances (concentration, way of adding the ammonia, &c.) exercise also some influence upon the composition and color of these hydrates. A small portion of the hydrates redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if after the addition of ammonia in excess heat is applied to the mixture the precipitation is complete.

5. *Carbonates of the alkalies* precipitate BASIC CARBONATE OF SESQUIOXIDE OF CHROMIUM, which redissolves with difficulty in excess of the precipitant.

6. *Carbonate of baryta* precipitates the whole of the sesquioxide as a GREENISH HYDRATE MIXED WITH BASIC SALT. The precipitation takes place in the cold, but is complete only after long-continued digestion.

N.B. to 3, 4, 5, and 6.—Tartaric and citric acids, sugar, and oxalic acid interfere more or less with the precipitation of violet or green solutions of oxide of chromium by ammonia, the first formed precipitates frequently redissolving entirely to red fluids after long standing. The above named acids generally prevent altogether the precipitation by carbonate of soda. In the presence of these acids also the precipitation by carbonate of baryta is incomplete.

7. If a solution of sesquioxide of chromium in solution of potassa or soda *is mixed with some brown peroxide of lead* in excess, and *the mixture is boiled a short time*, the sesquioxide of chromium is oxidized

to chromic acid. A yellow fluid is therefore obtained on filtering, which consists of a solution of CHROMATE OF OXIDE OF LEAD in solution of potassa or soda. Upon acidifying this fluid with acetic acid, the chromate of lead separates as a yellow precipitate (CHANCEL). Very minute traces of chromic acid may be detected in this fluid with still greater certainty by acidifying with hydrochloric acid, and bringing it in contact with peroxide of hydrogen and ether. Compare § 138.

8. The fusion of sesquioxide of chromium or of any of its compounds with *nitrate of soda and carbonate of soda*, or still better, with *chlorate of potassa and carbonate of soda*, gives rise to the formation of yellow ALKALINE CHROMATE, which dissolves in water to an intensely yellow fluid. For the reactions of chromic acid see § 138.

9. *Phosphate of soda and ammonia* dissolves sesquioxide of chromium and its salts, both in the oxidizing and reducing flame of the blowpipe, to clear beads of a faint yellowish-green tint, which upon cooling changes to EMERALD-GREEN. The sesquioxide of chromium and its salts show a similar reaction with *biborate of soda*. The Bunsen gas flame is used for the experiment, or the blowpipe flame.

## § 103.

*Recapitulation and remarks.*—The solubility of hydrate of alumina in solutions of potassa and soda, and its reprecipitation from the alkaline solutions by chloride of ammonium, afford a safe means of detecting alumina in the absence of sesquioxide of chromium. But if the latter substance is present, which is seen either by the color of the solution, or by the reaction with phosphate of soda and ammonia, it must be removed before alumina can be tested for. The separation of sesquioxide of chromium from alumina is effected the most completely by fusing 1 part of the mixed oxides with 2 parts of carbonate and 2 parts of chlorate of potassa, which may be done in a platinum crucible. The yellow mass obtained is boiled with water; by this process the whole of the chromium is dissolved as chromate of potassa, and part of the alumina as aluminate of potassa, the rest of the alumina remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish-yellow tint; if ammonia is then added to feebly alkaline reaction, the dissolved portion of the alumina separates.

The precipitation of sesquioxide of chromium effected by boiling its solution in solution of potassa or soda is also sufficiently exact if the ebullition is continued long enough; still it is often liable to mislead in cases where only little sesquioxide of chromium is present, or where the solution contains organic matter, even though in small proportion only. I have to call attention here to the fact that the solubility of hydrated sesquioxide of chromium in an excess of cold solution of potassa or soda is considerably impaired by the presence of other oxides (protoxides of manganese, nickel, cobalt, and more particularly sesquioxide of iron). If these oxides happen to be present in large excess they may even altogether prevent the solution of the hydrated sesquioxide of chromium in potassa or soda solution. Lastly, the influence of non-volatile organic acids, sugar, &c., upon the precipitation of alumina and sesquioxide of chromium by ammonia, &c., must be remembered. If organic substances are present therefore, ignite, fuse the residue with carbonate *and chlorate of potassa*, and proceed as directed before. In respect to

the detection of traces of alumina by an alcoholic solution of morin, compare GOPPELSRÖDER.*

*Special Reactions of the rarer Oxides of the third group.*

§ 104.

1. BERYLLA ($Be_2O_3$).

Berylla is a rare earth found in the form of a silicate in phenacite, and, with other silicates, in beryl, euclase, and some other rare minerals. It is a white, tasteless powder insoluble in water. The ignited earth dissolves slowly but completely in acids; it is readily soluble after fusion with bisulphate of potassa. The hydrate dissolves readily in acids. The compounds of berylla very much resemble the alumina compounds. The soluble berylla salts have a sweet astringent taste; their reaction is alkaline. The native silicates of berylla are completely decomposed by fusing with 4 parts of carbonate of soda and potassa. *Potassa, soda, ammonia,* and *sulphide of ammonium* throw down from solution of berylla salts a white flocculent hydrate, which is insoluble in ammonia, but dissolves readily in solution of potassa or soda, from which solution it is precipitated again by chloride of ammonium; the concentrated alkaline solutions remain clear on boiling, but from more dilute alkaline solutions almost the whole of the berylla separates upon continued ebullition (difference between berylla and alumina). Upon continued ebullition with *chloride of ammonium,* the freshly precipitated hydrate dissolves as chloride of beryllium, with expulsion of ammonia (difference between berylla and alumina.) *Carbonates of the alkalies* precipitate white carbonate of berylla, which redissolves in a great excess of the carbonates of the fixed alkalies, and in a much less considerable excess of carbonate of ammonia (most characteristic difference between berylla and alumina, but they cannot be completely separated in this way, as in the presence of berylla a certain quantity of alumina dissolves in carbonate of ammonia, JOY). Upon boiling these solutions basic carbonate of berylla separates, readily and completely from the solution in carbonate of ammonia, but only upon dilution and imperfectly from the solutions in carbonates of the fixed alkalies. *Carbonate of baryta* precipitates berylla completely upon cold digestion. *Oxalic acid* and *oxalates* do not precipitate berylla (difference between berylla and thoria, zirconia, yttria, erbia, protoxide of cerium, oxide of lanthanium, oxide of didymium). Berylla when fused with 2 parts of *acid fluoride of potassium,* dissolves in water acidified with hydrofluoric acid. (This reaction serves as a means of separating berylla from alumina, for when alumina is similarly treated it remains insoluble as fluoride of aluminium and potassium.) Moistened with solution of *nitrate of protoxide of cobalt,* the berylla compounds give gray masses upon ignition.

2. THORIA (Th O).

Thoria is a very rare earth found in thorite and monacite. It is white, while hot, yellow. The ignited earth is soluble only upon heating with a mixture of 1 part of concentrated sulphuric acid and 1 part of water; but it is not soluble in other acids, not even after fusion with alkalies. When evaporated with hydrochloric or nitric acid, the corresponding salts are left in a varnish-like form, which dissolves at once in water completely. Hydrochloric and nitric acids precipitate from such solutions the chloride or nitrate; even sulphuric acid may produce a precipitate in the solutions (BAHR). The moist hydrate dissolves readily in acids, the dried hydrate only with difficulty. Chloride of thorium is not volatile. Thorite (silicate of thoria) is decomposed by moderately concentrated sulphuric acid and also by concentrated hydrochloric acid. *Potassa, ammonia,* and *sulphide of ammonium* precipitate from solutions of thoria salts white hydrate, which is insoluble in an excess of the precipitant, even of potassa (difference between thoria and alumina and berylla). *Carbonate of potassa* and *carbonate of ammonia* precipitate basic carbonate of thoria, which readily dissolves in an excess of the precipitant in concentrated solutions, with difficulty in dilute solutions (difference between thoria and alumina). From the solution in carbonate of ammonia basic salt separates again even at 50°. *Carbonate of baryta* precipitates thoria completely. *Hydrofluoric acid* precipitates the fluoride which at first appears gelatinous, but after a little while pulverulent. The precipitate is insoluble in water and hydrofluoric acid. (Here thoria differs from alumina, berylla, zirconia, and titanic acid.)

* *Zeitschr. f.* anal. Chem. 7, 208.

*Oxalic acid* produces a white precipitate (here thoria differs from berylla and alumina). The precipitate does not dissolve in oxalic acid nor in dilute mineral acids, but it does dissolve in a solution of acetate of ammonia containing free acetic acid. (Here thoria differs from yttria and protoxide of cerium). The precipitate is insoluble in excess of oxalate of ammonia (difference between thoria and zirconia). *Sulphate of potassa* in concentrated solution precipitates thoria slowly but completely (here thoria differs from alumina and berylla). The precipitate consists of sulphate of potassa and thoria; it is insoluble in concentrated solution of sulphate of potassa; it dissolves with difficulty in cold and also in hot water, but readily on addition of some hydrochloric acid. On heating the neutral solution of sulphate of thoria in cold water, it separates in the form of a heavy white curdy precipitate (difference between thoria and alumina and berylla). This precipitate redissolves in cold water (in which it differs from titanic acid). *Hyposulphite of soda* precipitates from neutral or slightly acid solutions on boiling hyposulphite of thoria mixed with sulphur; the precipitation, however, is not quite complete (difference between thoria and yttria, erbia and oxide of didymium).

### 3. Zirconia ($ZrO_2$).

Found in zircon and some other rare minerals. A white powder insoluble in hydrochloric acid, soluble upon addition of water, after continued heating with a mixture of 2 parts of hydrated sulphuric acid and 1 part of water. The hydrate resembles hydrate of alumina, dissolving readily in hydrochloric acid when precipitated cold, and still moist, but with difficulty when precipitated hot, or after drying. The zirconia salts soluble in water redden litmus. The native silicates of zirconia may be decomposed by fusion with carbonate of soda. The finely elutriated silicate is fused at a high temperature, together with 4 parts of carbonate of soda. The fused mass gives to water silicate of soda, a sandy zirconate of soda being left behind, which is washed, and dissolves in hydrochloric acid. Zircon may easily be decomposed by fusion with acid fluoride of potassium at a red heat, fluosilicate of potassium and double fluoride of zirconium and potassium being produced. *Potassa, soda, ammonia,* and *sulphide of ammonium* precipitate from solutions of zirconia salts a flocculent hydrate, which is insoluble in an excess of the precipitant, even of soda and potassa (difference between zirconia and alumina and berylla), and is not dissolved even by boiling solution of chloride of ammonium (difference between zirconia and berylla). *Carbonates of potassa, soda,* and *ammonia,* throw down carbonate of zirconia as a flocculent precipitate, which redissolves in a large excess of carbonate of potassa, more readily in bicarbonate of potassa, and most readily in carbonate of ammonia (difference between zirconia and alumina), from which solution it precipitates again on boiling. *Oxalic acid* produces a bulky precipitate of oxalate of zirconia (difference between zirconia and alumina and berylla), which is insoluble in oxalic acid, soluble in hydrochloric acid, soluble in excess of oxalate of ammonia (difference between zirconia and thoria). A concentrated solution of *sulphate of potassa* speedily produces a white precipitate of sulphate of zirconia and potassa insoluble in excess of the precipitant (difference between zirconia and alumina and berylla), which—if precipitated cold—dissolves readily in a large proportion of hydrochloric acid, but is almost absolutely insoluble in water and in hydrochloric acid if precipitated hot (difference between zirconia and thoria and protoxide of cerium). Sulphate of zirconia is difficultly soluble in cold water, readily soluble in hot water (difference between zirconia and thoria). *Carbonate of baryta* does not precipitate zirconia salts completely, even upon boiling. *Hydrofluoric acid* does not precipitate zirconia salts (difference between zirconia and thoria and yttria). *Hyposulphite of soda* precipitates zirconia salts (difference between zirconia and yttria, erbia, and oxide of didymium). The separation of the hyposulphite of zirconia takes place on boiling even in the presence of 100 parts of water to 1 part of the oxide (difference between zirconia and protoxide of cerium and oxide of lanthanium). *Turmeric paper* dipped into solutions of zirconia slightly acidified with hydrochloric or sulphuric acid, acquires a brownish red color after drying (difference between zirconia and thoria). In the presence of titanic acid, which also has the effect of turning turmeric paper brown, treat the acid solution with zinc first, to reduce the titanic acid to oxide of titanium, the solution of which does not affect turmeric paper (Pisani).

### 4. Yttria (Y O).

Yttria is a rare earth found in gadolinite, orthite, yttro-tantalite. When pure it is pale yellowish-white, when ignited in the oxidizing flame it emits a white light (difference between yttria and erbia) without fusing or volatilizing. In nitric, hydrochloric, and *dilute sulphuric acid* it is difficultly soluble in the cold, but on warming it dissolves *completely after some* time. The solutions are colorless, and likewise the salts, they

have an acid reaction and a sweetish astringent taste. Yttria does not combine with water. Yttria under no circumstances yields a spectrum, nor do the solutions of its salts show any absorption bands (Bahr and Bunsen). Anhydrous chloride of yttrium is not volatile (difference between yttria and alumina, berylla and zirconia). *Potassa* precipitates white hydrate, which is insoluble in an excess of the precipitant (difference between yttria and alumina and berylla). *Ammonia* and *sulphide of ammonium* produce the same reaction. Presence of a small quantity of chloride of ammonium will not prevent the precipitation by sulphide of ammonium; but in presence of a large excess of chloride of ammonium sulphide of ammonium fails to precipitate solutions of salts of yttria. *Carbonates of the alkalies* produce a white precipitate, which dissolves with difficulty in carbonate of potassa, but more readily in bicarbonate of potassa and in carbonate of ammonia, though by no means so readily as the corresponding berylla precipitate. The solution of the pure hydrate in carbonate of ammonia deposits on boiling the whole of the yttria; if chloride of ammonium is present at the same time, this is decomposed upon continued heating, with separation of ammonia, and the precipitated yttria redissolves as chloride of yttrium. Saturated solutions of carbonate of yttria in carbonate of ammonia have a tendency to deposit carbonate of yttria and ammonia, which should be borne in mind. *Oxalic acid* produces a white precipitate (difference between yttria and alumina and berylla). The precipitate does not dissolve in oxalic acid, but it dissolves with difficulty in dilute hydrochloric acid, and it is partially dissolved by boiling with oxalate of ammonia. *Sulphate of yttria and potassa* dissolves readily in water and in a solution of sulphate of potassa (difference between yttria and thoria, zirconia and the bases of cerite). *Carbonate of baryta* produces no precipitate in the cold (difference between yttria and alumina, berylla, thoria, oxide of cerium, and oxide of didymium), on boiling even the precipitation is incomplete. *Turmeric paper* is not altered by acidified solutions of salt of yttria (difference between yttria and zirconia). *Tartaric acid* does not interfere with the precipitation of yttria by alkalies (characteristic difference between yttria and alumina, berylla, thoria, and zirconia). The precipitate is tartrate of yttria. The precipitation ensues only after some time, but it is complete. *Hyposulphite of soda* does not precipitate yttria (difference between yttria and alumina, thoria, zirconia, and titanic acid). *Hydrofluoric acid* produces a precipitate (here yttria differs from alumina, berylla, zirconia, and titanic acid); the precipitate is gelatinous, insoluble in water and hydrofluoric acid; before ignition it will dissolve in mineral acids, after ignition it is decomposed only by strong sulphuric acid. A cold saturated solution of the *sulphate becomes turbid when heated* to between 30° and 40°; on boiling almost the whole of the salt separates. Yttria gives clear colorless beads with *borax* and *phosphate of soda and ammonia* in both the outer and inner flame (difference between yttria and protoxide of cerium and oxide of didymium).

### 5. Oxide of Erbium (Er O).

Oxide of erbium accompanies yttria in gadolinite.* It is distinguished by its fine rose color, it does not alter on ignition in hydrogen, and does not fuse in the highest white heat. When strongly heated in the form of a spongy mass, it glows with an intense green light. In *nitric*, *hydrochloric*, and *sulphuric acid* it dissolves with difficulty, but on warming completely. Its *salts* have a more or less bright rose tint, which is stronger generally with the hydrated than with the anhydrous salts, they have an acid reaction and a sweetish astringent taste. The oxide of erbium does not combine directly with water. The sulphate when hydrated dissolves in water with difficulty, when anhydrous it dissolves readily. The basic nitrate ($2\,Er\,O,\,N\,O_5 + 3$ aq.) forms bright rose colored, needle-shaped crystals, which are difficultly soluble in nitric acid, decomposed by water into nitric acid and gelatinous hyperbasic salt, and yield the oxide on ignition. The oxalate is a rose colored, heavy sandy powder. Finally the oxide of erbium is most decisively characterized by the *absorption-spectrum* which is given by the solutions of its salts. Of the absorption bands $\alpha$ lies between 71 and 74, $\beta$ between 64·5 and 65·5, $\gamma$ between 32·6 and 38·0, $\delta$ between 85 and 91 on the spectrum table. If the solid ignited earth is saturated with not too concentrated phosphoric acid and reignited, a direct spectrum is obtained, the bright lines of which coincide with the dark ones of the absorption-spectrum. With *borax* and *microcosmic*

* Mosander imagined that he had separated also another earth, namely, the oxide of terbium. Popp considered both earths to be mixtures of yttria with oxide of cerium and oxide of didymium. Delafontaine defended Mosander's view. However Bahr and Bunsen *found in gadolinite only one* other earth besides yttria, namely, oxide of *erbium (Annal. d. Chem. u. Pharm. 137, 1).*

*salt* the oxide of erbium gives beads which are clear and colorless when hot and also after cooling (difference between oxide of erbium and protoxide of cerium and oxide of didymium).

In the separation of oxide of erbium from yttria, which show a great likeness to each other in their deportment to reagents, BAHR and BUNSEN make use of the different behaviour of the nitrates when heated. The separation is however not complete unless the process is repeated over and over again, compare *op. cit.*, p. 3.

### 6. OXIDES OF CERIUM.

Cerium is a rare metal; it is found in the form of protoxide in cerite, orthite, &c. It forms three oxides, the protoxide (Ce O), the sequioxide ($Ce_2O_3$) and the peroxide ($Ce O_2$) which are capable of entering into combination with each other. The hydrate of the protoxide is white, but turns yellow upon exposure to the air, by absorption of oxygen. By ignition in the air it is converted into orange-red or red sesquioxide (difference between it and the preceding earths). Hydrate of protoxide of cerium dissolves readily in acids. Ignited sesquioxide of cerium containing oxide of lanthanium and didymium dissolves readily in hydrochloric acid, with evolution of chlorine: in the pure state it dissolves very slightly in boiling hydrochloric acid, except upon addition of some alcohol (difference between oxide of cerium and thoria and zirconia); the solution contains protochloride. The sesquioxide dissolves in concentrated sulphuric acid, although with difficulty; it is hardly attacked by nitric acid. The sesquioxide obtained from the oxalate when evaporated with nitric acid yields a basic salt, which gives an emulsion with water, and is not completely soluble in very considerable quantities of water (difference from thoria). The salts of protoxide of cerium are colorless, occasionally with a slight shade of amethyst red; the soluble protoxide salts redden litmus. Protochloride of cerium is not volatile (difference from alumina, berylla, and zirconia). The sulphate does not dissolve entirely in boiling water. Cerite (hydrated silicate of protoxide of cerium 2 [Ce O, La O, Di O] $Si O_2 + 2$ aq.) does not dissolve in aqua regia; but is decomposed by fusion with carbonate of soda, and also by concentrated sulphuric acid. *Potassa* precipitates white hydrate, which turns yellow in the air, and does not dissolve in an excess of the precipitant (difference from alumina and berylla). *Ammonia* precipitates basic salt, which is insoluble in an excess of the precipitant. *Carbonates of the alkalies* produce a white precipitate, which dissolves sparingly in an excess of carbonate of potassa, somewhat more readily in carbonate of ammonia. *Oxalic acid* produces a white precipitate; the precipitation is complete even in moderately acid solutions (difference from alumina and berylla). The precipitate is not dissolved by oxalic acid; but it dissolves in a large proportion of hydrochloric acid. A saturated solution of *sulphate of potassa* precipitates, even from somewhat acid solutions, white sulphate of potassa and protoxide of cerium (difference from alumina and berylla), which is difficultly soluble in cold water, readily soluble in hot water and altogether insoluble in a saturated solution of sulphate of potassa (difference from yttria). The precipitate may be dissolved by boiling with a large quantity of water, to which some hydrochloric acid has been added. *Carbonate of baryta* precipitates solutions of cerium salts slowly, but completely upon long-continued action. *Tartaric acid* prevents precipitation by ammonia (difference from yttria) but not by potassa. *Hyposulphite of soda* does not precipitate cerium, even on boiling with very concentrated solutions. The precipitated sulphur only carries down traces of the salt with it. If we conduct *chlorine* through a solution of protoxide of cerium not too acid and mixed with acetate of soda, or if we add *hypochlorite of soda* to such a solution, all the cerium is precipitated as light yellow peroxide (free from didymium and lanthanium, POPP). If a salt of protoxide of cerium be dissolved in nitric acid, with addition of an equal volume of water, and if a small quantity of *binoxide of lead* be added, and the liquid be boiled for some minutes, the solution turns yellow, even if only small quantities of cerium be present. On evaporating this solution to dryness, heating the residue till a portion of the acid escapes, and treating it with water acidified with nitric acid, no cerium will be dissolved, but any didymium and lanthanium present will be dissolved (GIBBS). Solutions of salts of sesquioxide of cerium are precipitated in the cold by *carbonate of baryta*. *Hyposulphite of soda* precipitates a solution of nitrate of sesquioxide of cerium. *Borax* and *phosphate of soda and ammonia* dissolve cerium oxides in the outer flame to yellowish red beads (difference from the preceding earths); the coloration gets fainter on cooling, and often disappears altogether. In the inner flame colorless beads are obtained.

### 7. OXIDE OF LANTHANIUM.

*This oxide is* generally found associated with protoxide of cerium. It is white and

remains unaltered by ignition in the air (difference from protoxide of cerium). In contact with cold water it is slowly converted into a milk-white hydrate; with hot water the conversion is rapid. The oxide and its hydrate change the color of reddened litmus-paper to blue; they dissolve in boiling solution of chloride of ammonium, also in dilute acids. Oxide of lanthanium in this resembles magnesia. The salts of oxide of lanthanium are colorless; the saturated solution of sulphate of oxide of lanthanium in cold water deposits a portion of the salt already at 30° (difference from protoxide of cerium). *Sulphate of potassa, oxalic acid,* and *carbonate of baryta* give the same reactions as with protoxide of cerium. *Potassa* precipitates hydrate, which is insoluble in an excess of the precipitant, and does not turn brown in the air. *Ammonia* precipitates basic salts, which pass milky through the filter on washing. The precipitate produced by carbonate of ammonia is insoluble in an excess of the precipitant (difference from protoxide of cerium). If a cold dilute solution of acetate of oxide of lanthanium is supersaturated with ammonia, the slimy precipitate repeatedly washed with cold water, and a little *iodine* in powder added, a blue coloration makes its appearance, which gradually pervades the entire mixture (characteristic difference between oxide of lanthanium and the other earths).

### 8. Oxide of Didymium.

This oxide, like the oxide of lanthanium and in conjunction with it, is found associated with the protoxide of cerium. After intense ignition it appears white, moistened with nitric acid and feebly ignited dark-brown, after intense ignition again white. In contact with water it is slowly converted into hydrate; it rapidly attracts carbonic acid; its reaction is not alkaline; it dissolves readily in acids. The concentrated solutions have a reddish or a faint violet color. The nitrate on heating is first converted into a basic salt ($4\,Di\,O, N\,O_5 + 5$ aq., difference from lanthanium) which is gray when hot and also when cold (difference from erbium). The chloride is not volatile. The saturated solution of the sulphate deposits salt, not at 30°, but upon boiling. *Potassa* precipitates hydrate, which is insoluble in an excess of the precipitant, and does not alter in the air. *Ammonia* precipitates basic salt, which is insoluble in ammonia, but slightly soluble in chloride of ammonium. *Carbonates of the alkalies* produce a copious precipitate, which is insoluble in an excess of the precipitant, even in an excess of carbonate of ammonia (difference from protoxide of cerium), but dissolves slightly in concentrated solution of chloride of ammonium. *Oxalic acid* precipitates salts of oxide of didymium almost completely; the precipitate is difficultly soluble in cold hydrochloric acid, but dissolves in that menstruum upon application of heat. *Carbonate of baryta* precipitates oxide of didymium from its solutions slowly (more slowly than protoxide of cerium and oxide of lanthanium), and never completely. A concentrated solution of *sulphate of potassa* precipitates didymium solutions more slowly and less completely than protoxide of cerium solutions. The precipitate is insoluble in solution of sulphate of potassa, and in water (Delafontaine), but it dissolves in hot hydrochloric acid with difficulty. *Hyposulphite of soda* does not precipitate solutions of didymium. Oxide of didymium gives with *borax* in both flames a nearly colorless bead, which in the presence of large quantities has a faint amethyst-red tinge. *Phosphate of soda and ammonia* dissolves the oxide in the reducing flame to an amethyst-red bead inclining to violet. With *carbonate of soda* in the outer flame a grayish-white mass is obtained (difference from manganese). The *absorption-spectrum* given by the solutions of the salts is peculiarly characteristic for didymium. This was first described by Gladstone, and afterwards by O. L. Erdmann and Delafontaine. Bahr and Bunsen have laid down the exact position of the bands (Zeitschr. f. anal. Chem. 5, 110). A direct spectrum may also be obtained from didymium as from erbium, but it is by no means well marked.

For the separation of cerium from lanthanium and didymium, one of the following methods may be used:—*a.* Nearly neutralize the solution of the three metals, if acid, without allowing any permanent precipitate to form, add a sufficient quantity of acetate of soda and an excess of hypochlorite of soda, and boil for some time; the cerium will fall as peroxide, while lanthanium and didymium remain in solution. (Popp, Ann. d. Chem. u. Pharm., 131, 360). *b.* Precipitate the metals with potassa, wash, suspend the precipitate in potassa, and pass chlorine. Lanthanium and didymium dissolve; the peroxide of cerium remains behind. (Damour and St. Claire Deville, Compt. Rend., 59, 272). *c.* Dissolve in a large excess of nitric acid; boil with peroxide of lead; evaporate the orange colored solution to dryness, and heat the residue till a portion of the acid escapes; treat with water acidulated with nitric acid, and separate the insoluble basic nitrate of sesquioxide of cerium from the solution which contains all

the lanthanium and didymium. (GIBBS, Zeitschr. f. anal. Chem., 3, 396). In using the last method, before proceeding with the residue or solution, the lead must be first separated by sulphuretted hydrogen. *d.* Heat the chromates to 110°, and treat with hot water to extract the undecomposed compounds of lanthanium and didymium. The cerium remains behind as insoluble sesquioxide (PATTINSON and CLARK, Chem. News, 16, 259). From the solution of lanthanium and didymium obtained by one or other of the above methods, the bases are precipitated with oxalate of ammonia, the oxalates are ignited, and the oxides thus obtained are treated with dilute nitric acid. If the separation of cerium was incomplete, the remainder of the cerium will here remain behind. The solution is evaporated in a dish with a flat bottom to dryness and heated to 400°–500°. The salts fuse; nitrous fumes escape. The residue is treated with hot water, which dissolves the nitrate of lanthanium, leaving behind gray basic nitrate of didymium. By a repetition of the evaporation, &c., the two bases may be satisfactorily separated. (DAMOUR and ST. CLAIRE DEVILLE.) Another method of separation, which is however less complete, consists in converting the didymium and lanthanium into sulphates, making a saturated solution of the dry salts in water at 5° or 6°, and heating the solution to 30°, when the sulphate of lanthanium is for the most part thrown down and the sulphate of didymium is for the most part held in solution. For another method of separating lanthanium and didymium, which requires the presence of a considerable quantity of cerium, compare CL. WINKLER (Zeitschr. f. anal. Chem. 4, 417.)

### 9. TITANIC ACID.

Titanium forms two oxides, sesquioxide of titanium ($Ti_2O_3$) and titanic acid ($Ti O_2$). The latter is somewhat more frequently met with in analysis. It is found in the free state in rutile and anatase, in combination with bases in titanite, titaniferous iron, &c. It is found in small proportions in many iron ores, in clays, and generally in silicates, consequently also in blast furnace slags. The small copper-colored cubes which are occasionally found in such slags consist of a combination of cyanide of titanium with nitride of titanium. Feebly ignited titanic acid is white; it transiently acquires a lemon tint when heated; very intense ignition gives a yellowish or brownish tint to it. It is infusible, insoluble in water, and its specific gravity is 3·9 to 4·25. The chloride ($Ti Cl_2$) is a colorless volatile fluid, fuming strongly in the air.

*a. Deportment with acids and reactions of acid solutions of titanic acid.*—Ignited titanic acid is insoluble in acids, except in hydrofluoric acid and in concentrated sulphuric acid. If the solution in hydrofluoric acid is evaporated with sulphuric acid, no fluoride of titanium will volatilize (difference from silicic acid.) With bisulphate of potassa it gives upon sufficiently long-continued fusion a clear mass, which is completely soluble in a large proportion of cold water. Titanic is very easily obtained in the state of a clear solution, by fusing with acid fluoride of potassium and dissolving the fusion in dilute hydrochloric acid. The fluoride of potassium and titanium is difficultly soluble in water, 1 part requiring 96 parts at 14°. Hydrate of titanic acid dissolves, both moist and when dried without the aid of heat, in dilute acids, especially in hydrochloric and sulphuric acids. All the solutions of titanic acid in hydrochloric or sulphuric acid, but more particularly the latter, when subjected in a highly dilute state to *long-continued boiling*, deposit titanic acid as a white powder (hydrated metatitanic acid) insoluble in dilute acids. Presence of much free acid retards the separation and diminishes the quantity of the precipitate. The precipitate which separates from the hydrochloric acid solution may, indeed, be filtered, but it will pass milky through the filter upon washing, except an acid or chloride of ammonium be added to the washing water. *Solution of potassa* throws down from solutions of titanic acid in hydrochloric or sulphuric acid hydrate of titanic acid as a bulky white precipitate, which is insoluble in an excess of the precipitant; *ammonia*, *sulphide of ammonium*, and *carbonate of baryta* act in the same way. The precipitate, thrown down cold and washed with cold water, is soluble in hydrochloric acid and in dilute sulphuric acid; presence of tartaric acid prevents its formation. *Ferrocyanide of potassium* produces in acid solutions of titanic acid a dark-brown precipitate; *infusion of galls* a brownish precipitate, which speedily turns orange-red. On boiling a solution of titanic acid with *hyposulphite of soda*, the whole of the titanic acid is thrown down. *Phosphate of soda* throws down the titanic acid almost completely as phosphate of titanic acid even from solutions containing much hydrochloric acid. The washed precipitate consists of $2 Ti O_2, PO_5$ (MERZ). *Zinc or tin* produces after some time a pale violet or blue coloration; subsequently a blue precipitate, which gradually becomes white. The coloration is caused by the reduction of the titanic acid to sesquioxide of titanium. If to the blue but still clear solution potassa or ammonia is added, blue hydrated sesquioxide of titanium separates, which is gradually converted into white hydrated titanic acid with decomposition of water.

The reduction of titanic acid in hydrochloric solution takes place also in the presence of fluoride of potassium (difference from niobic acid), the fluid becoming bright green. The solutions of chloride of titanium in water have properties which vary according to their preparation with hot or cold water. The solution prepared with cold water is not precipitated by sulphuric acid, nor by hydrochloric, nor by nitric, it is precipitated by phosphoric acid, arsenic acid, or iodic acid; but if the solution be boiled only for a few seconds it becomes slightly opalescent, and so far modified that hydrochloric and nitric acids produce white precipitates in it which are insoluble in excess of the acids, sulphuric acid also precipitates it, but an excess redissolves the precipitate. The solution prepared in the cold contains titanic acid, the boiled solution contains metatitanic acid. The difference also attaches to the hydrates. (R. Weber, Pogg. Ann. 120, 287.)

*b. Reactions with alkalies.*—Recently precipitated hydrate of titanic acid is almost absolutely insoluble in solution of potassa. If titanic acid is fused with *hydrate of potassa*, and the fused mass treated with water, the solution contains a little more titanic acid. By fusion with *carbonates of the alkalies* neutral titanates of the alkalies are formed, with expulsion of carbonic acid. Water extracts from the fused mass free alkali and alkaline carbonate, leaving behind acid titanate of alkali which dissolves in hydrochloric acid. Titanic acid mixed with charcoal gives upon ignition in a *stream of chlorine* chloride of titanium as a volatile liquid, which emits copious fumes in the air. *Phosphate of soda and ammonia* dissolves titanic acid in the point of the outer blowpipe flame to a colorless bead but with difficulty, in the outer flame in front of the point of the inner flame titanic acid dissolves readily and in considerable quantity. If the clear and colorless bead is again held in the point of the outer flame, it becomes opaque if sufficiently saturated, and by continued action of the flame titanic acid will separate in microscopic crystals of the form of anatase (G. Rose). If the bead is held in a good reducing flame for some time, it will appear yellow while hot, red while cooling, and violet when cold. The reduction is promoted by the addition of a little tin. If some protosulphate of iron is added, the bead obtained in the reducing flame will appear blood-red.

### 10. Tantalic Acid.*

Tantalum forms with oxygen the tantalic acid, $Ta O_2$ (Ta = 182), the existence of a lower oxide is probable, but its formula and properties have not been made out. Tantalic acid occurs in columbite and tantalite (almost always in conjunction with niobic acid). Tantalic acid is white, pale yellowish when hot (difference from $Ti O_2$), when separated in the wet way it contains water of hydration. The anhydrous acid has a specific gravity of 7·6—8·01. Tantalic acid is not reduced by ignition in a current of *hydrogen*. It combines with acids as well as with bases.

*a. Acid solutions.*—When the acid is intimately mixed with charcoal and ignited in a current of dry *chlorine*, the chloride of tantalum ($Ta Cl_5$) is formed. The latter is yellow, solid, fusible, and can be sublimed; it is completely decomposed by water, with separation of tantalic acid; it is entirely soluble in sulphuric acid, almost soluble in hydrochloric acid, and partially soluble in potassa solution. If titanic acid is present, on treating the mixture of acids and charcoal with the current of chlorine, the chloride of titanium will be formed and will fume strongly in the air. Hydrated tantalic acid dissolves in *hydrofluoric acid*, the solution when mixed with fluoride of potassium yields a very characteristic salt in fine needles ($2 K F, Ta F_5$), which is distinguished by its difficult solubility in water acidified with hydrofluoric acid (1 of the acid to 150 or 200 of water). Hydrochloric and concentrated sulphuric acid do not dissolve the ignited acid. With bisulphate of potassa it fuses to a colorless mass; if this is treated with water, the tantalic acid combined with sulphuric acid remains undissolved (difference between tantalic acid and titanic acid, but cannot be made the ground of a method of separation). When ignited in an atmosphere of carbonate of ammonia, the sulphate of tantalic acid is converted into pure tantalic acid. If a solution of alkaline tantalate is mixed with hydrochloric acid in excess, the first-formed precipitate redissolves to an opalescent fluid. *Ammonia* and *sulphide of ammonium* precipitate from this fluid the hydrate or an acid tantalate of ammonia, but tartaric acid prevents the precipitation. *Sulphuric acid* precipitates sulphate of tantalic acid from the opalescent fluid. When acid solutions of tantalic acid are brought into contact with *zinc*, no blue coloration is observed (difference between tantalic acid and niobic acid).

*b. Behaviour to alkalies.*—By continued fusion with *hydrate of potassa* tantalate of

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* The results of the recent investigations on tantalic and niobic acids by Marignac, Blomstrand, Deville and Troost, and Hermann will be found in Zeitschr. f. anal. Chem. 5, 334 *et seq.* and 7, 104 *et seq.*

potassa is formed; the fused mass dissolves in water. By fusion with *hydrate of soda* a turbid mass is obtained; a little water poured on this mass will dissolve out the excess of soda, leaving the whole of the tantalate of soda undissolved, as this latter sal is insoluble in solution of soda; but the tantalate of soda will dissolve in water after the removal of the excess of soda. Solution of soda throws down from this solution the tantalate of soda; if the precipitant be added slowly, the form of the precipitate is crystalline. Carbonic acid throws down from solutions of tantalates of the alkalies acid salts, which are not dissolved by boiling with solution of carbonate of soda. *Sulphuric acid* throws down even from dilute solutions of tantalates of the alkalies sulphate of tantalic acid; *ferrocyanide of potassium* and *infusion of galls* produce precipitates only in acidified solutions; the precipitate produced by the former is yellow, by the latter light brown. *Phosphate of soda and ammonia* dissolves tantalic acid to a colorless bead, which is colorless also when hot, remains colorless even in the inner flame, and does not acquire a blood-red tint by addition of sulphate of protoxide of iron (difference between tantalic acid and titanic acid).

### 11. Niobic Acid.

Niobium (Nb = 94) combines with oxygen in several proportions. $NbO_2$, $NbO_4$ are oxides, $Nb_2O_5$ (niobic acid) is an acid. It is occasionally found in columbite, samarskite, &c., and it is usually accompanied by tantalic acid. It is white, but turns transiently yellow when ignited (difference between niobic acid and tantalic acid). Its specific gravity lies between 4·37 to 4·53 (difference between niobic acid and tantalic acid). By strong ignition in *hydrogen* the niobic acid is converted into black $NbO_2$. Niobic acid combines both with bases and acids.

a. *Acid solutions of niobic acid.*—Concentrated *sulphuric acid* dissolves the acid on heating, unless it has been too strongly ignited. On the addition of much cold water, a clear solution is obtained. On fusing with *bisulphate of potassa* it dissolves readily to a colorless mass, and on treating the fusion with boiling water niobic acid containing sulphuric acid remains undissolved, which however is readily soluble in hydrofluoric acid, see below. By mixing niobic acid intimately with charcoal and treating with a current of *chlorine*, a mixture is obtained of white infusible difficultly volatile oxychloride ($Nb_2O_3Cl_2$) and yellow more volatile chloride ($NbCl_5$). Treated with water both compounds give turbid fluids, in which a portion of the niobic acid is separated, but the larger portion is dissolved. By boiling with hydrochloric acid and afterwards adding water the compounds give clear solutions, which are not precipitated by boiling or by sulphuric acid in the cold (difference from chloride of tantalum). By igniting niobic acid in the vapor of chloride of niobium the oxychloride is formed (difference from tantalic acid). From the acid solutions of niobic acid *ammonia* and *sulphide of ammonium* throw down hydrate of niobic acid containing ammonia; this and generally the unignited forms of niobic acid dissolve in *hydrofluoric acid*. The solution when mixed with fluoride of potassium gives fluoride of potassium and niobium ($KF, NbF_5$) when hydrofluoric acid is in excess, otherwise it gives a combination of fluoride of potassium and oxyfluoride of niobium ($KF, NbO_2F_3$). The latter salt is also obtained when niobate of potassa is dissolved in hydrofluoric acid; it is readily soluble in cold water, one part dissolving in 12·5 parts (difference from fluoride of potassium and titanium, which requires 96 parts of water, and from fluoride of potassium and tantalum which requires 200 parts of water). On digesting a hydrochloric or sulphuric acid solution of niobic acid with *zinc* or *tin*, it acquires a blue and generally also a brown color, in consequence of the reduction of the niobic acid to lower oxides. In the presence of alkaline fluorides the reduction does not take place (difference between niobic acid and titanic acid).

b. *Alkaline solutions.*—With *hydrate of potassa* niobic acid fuses to a clear mass, soluble in water. To *hydrate of soda* niobic acid shows the same deportment as tantalic acid. From the solution of niobate of potassa, solution of *soda* precipitates an almost insoluble niobate of soda. On boiling a solution of niobate of potassa with *bicarbonate of potassa* an almost insoluble acid niobate of potassa is thrown down. On fusing niobic acid with *carbonate of soda* and boiling the fusion with water, a crystalline acid niobate of soda remains undissolved. *Carbonic acid*, when passed into solution of niobate of soda precipitates all the niobic acid as an acid salt. *Phosphate of soda and ammonia* dissolves niobic acid readily; the bead held in the outer flame appears colorless as long as it is hot; the bead held in the inner flame has a violet, blue, or brown color, according to the quantity of the acid present, and a red color on the addition of sulphate of protoxide of iron.

*For the best methods of detecting the whole of the members of the third group in presence of each other, see* Part II., Section III.

## § 105.

### FOURTH GROUP.

More common oxides:—OXIDE OF ZINC, PROTOXIDE OF MANGANESE, PROTOXIDE OF NICKEL, PROTOXIDE OF COBALT, PROTOXIDE OF IRON, SESQUIOXIDE OF IRON.

Rarer oxides:—SESQUIOXIDE OF URANIUM, PROTOXIDE OF THALLIUM, OXIDE OF INDIUM, OXIDES OF VANADIUM.

*Properties of the Group.*—The solutions of the oxides of the fourth group, if containing a stronger free acid, are not precipitated by hydrosulphuric acid; nor are neutral solutions, at least not completely. But alkaline solutions are completely precipitated by hydrosulphuric acid; and so are other solutions if a sulphide of an alkali metal is used as the precipitant, instead of hydrosulphuric acid.* The precipitated metallic sulphides corresponding to the several oxides are insoluble in water; some of them are readily soluble in dilute acids; others (sulphide of nickel and sulphide of cobalt) dissolve only with very great difficulty in these menstrua. Some of them are insoluble in sulphides of the alkali metals, others (nickel) are sparingly soluble in them, under certain circumstances, whilst others again (vanadium) are completely soluble. The oxides of the fourth group differ accordingly from those of the first and second groups in this, that their solutions are precipitated by sulphide of ammonium, and from those of the third group inasmuch that the precipitates produced by sulphide of ammonium are sulphides, and not hydrated oxides, as is the case with alumina, sesquioxide of chromium, &c.

### *Special Reactions of the more common Oxides of the fourth group.*

## § 106.

### *a.* OXIDE OF ZINC (Zn O).

1. METALLIC ZINC is bluish-white and very bright; when exposed to the air, a thin coating of basic carbonate of zinc forms on its surface. It is of medium hardness, malleable at a temperature of between 100° and 150°, but otherwise more or less brittle; it fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Zinc dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen gas; in dilute nitric acid, with evolution of nitrous oxide; in more concentrated nitric acid, with evolution of nitric oxide.

2. The OXIDE OF ZINC and its HYDRATE are white powders, which are insoluble in water, but dissolve readily in hydrochloric, nitric, and sulphuric acids. The oxide of zinc acquires a lemon-yellow tint when heated, but it resumes its original white color upon cooling. When ignited before the blowpipe, it shines with considerable brilliancy.

3. The SALTS OF OXIDE OF ZINC are colorless; part of them are soluble in water, the rest in acids. The neutral salts of zinc which are soluble in water redden litmus-paper, and are readily decomposed by heat,

* *Vanadic acid behaves in a peculiar way to sulphide of ammonium, see § 113, d.*

with the exception of sulphate of zinc, which can bear a dull red heat without undergoing decomposition. Chloride of zinc is volatile at a red heat.

4. *Hydrosulphuric acid* precipitates from neutral solutions a portion of the metal as white hydrated sulphide of zinc (Zn S). In acid solutions this reagent fails altogether to produce a precipitate if the free acid present is one of the stronger acids; but from a solution of oxide of zinc in acetic acid it throws down the whole of the zinc, even if the acid is present in excess.

5. *Sulphide of ammonium* throws down from neutral and hydrosulphuric acid from alkaline solutions the whole of the metal as hydrated SULPHIDE OF ZINC, in the form of a white precipitate. Chloride of ammonium greatly promotes the separation of the precipitate. From very dilute solutions the precipitate separates only after long standing. This precipitate is not redissolved by an excess of sulphide of ammonium, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid. It is insoluble in acetic acid.

6. *Potassa and soda* throw down HYDRATED OXIDE OF ZINC (Zn O, H O), in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. Upon boiling these alkaline solutions they remain, if concentrated, unaltered; but from dilute solutions nearly the whole of the oxide of zinc separates as a white precipitate. Chloride of ammonium added to alkaline solutions, not containing a large excess of potassa or soda, produces a white precipitate of hydrated oxide of zinc, which, however, redissolves on addition of more chloride of ammonium (difference between oxide of zinc and alumina).

7. *Ammonia* also produces in solutions, if they do not contain a large excess of free acid, a precipitate of HYDRATED OXIDE OF ZINC, which readily dissolves in an excess of the precipitant. The concentrated solution turns turbid when mixed with water. On boiling the concentrated solution part of the oxide of zinc separates immediately; on boiling the dilute solution all the oxide of zinc precipitates. Ammonia salts interfere with these precipitations more or less.

8. *Carbonate of soda* produces a precipitate of BASIC CARBONATE OF ZINC ($3\,[Zn\,O, H\,O] + 2\,[Zn\,O, C\,O_2] + 4$ aq.), which is insoluble in an excess of the precipitant. Presence of salts of ammonia in great excess prevents the formation of this precipitate.

9. *Carbonate of ammonia* also produces the same precipitate of BASIC CARBONATE OF ZINC as carbonate of soda; but this precipitate redissolves upon further addition of the precipitant. On boiling the dilute solution oxide of zinc precipitates. Ammonia salts interfere with this precipitation more or less.

N.B. Non-volatile organic acids more or less interfere with the precipitation of solutions of zinc, by the caustic and carbonated alkalies. Sugar does not prevent the precipitations.

10. *Carbonate of baryta* fails to precipitate solutions of salts of zinc in the cold, with the exception of the sulphate.

11. *Ferrocyanide of potassium* throws down FERROCYANIDE OF ZINC (2 Zn, Cfy) as a white slimy precipitate, somewhat soluble in excess of the precipitant, insoluble in hydrochloric acid.

12. *Ferricyanide of potassium* throws down FERRICYANIDE OF ZINC

(3 Zn, Cfdy) as a brownish orange-yellow precipitate, soluble in hydrochloric acid and in ammonia.

13. If a mixture of oxide of zinc or one of its salts with *carbonate of soda* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a slight coating of OXIDE OF ZINC, which presents a yellow color whilst hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame. The METALLIC INCRUSTATION obtained according to p. 25 is black with a brown edge, the INCRUSTATION OF OXIDE is white, and therefore invisible upon porcelain. It may be dissolved in nitric acid and examined according to 14.

14. If oxide of zinc or one of the salts of zinc is moistened with solution of *nitrate of protoxide of cobalt*, and then heated before the blowpipe, an unfused mass is obtained of a beautiful GREEN color: this mass is a compound of oxide of zinc with protoxide of cobalt. If therefore in the first experiment described in 13 the charcoal is moistened around the little cavity with solution of cobalt, the coating appears *green when cold*. This test may be applied with great delicacy by mixing the solution to be tested with a very little of the cobalt solution (not enough to give a bright red color), adding carbonate of soda in slight excess, boiling, filtering off, washing, and igniting on platinum foil. On triturating the residue the green color may be distinctly and readily observed (BLOXAM).

## § 107.

### *b.* PROTOXIDE OF MANGANESE (Mn O).

1. METALLIC MANGANESE is whitish-gray, dull, very hard, brittle, and fuses with very great difficulty. It oxidizes rapidly in the air, and in water with evolution of hydrogen, and crumbles to a dark gray powder. It dissolves readily in acids, the solutions contain protoxide.

2. PROTOXIDE OF MANGANESE is light green; the hydrated protoxide is white. The former smoulders to brown protosesquioxide when heated in the air, the latter even at the ordinary temperature rapidly absorbs oxygen from the air and passes into brown hydrated protosesquioxide. They are readily soluble in hydrochloric, nitric, and sulphuric acids. All the HIGHER OXIDES OF MANGANESE without exception dissolve to protochloride, with evolution of chlorine, when heated with hydrochloric acid; to sulphate of protoxide, with evolution of oxygen, when heated with concentrated sulphuric acid.

3. The SALTS OF PROTOXIDE OF MANGANESE are colorless or pale red; part of them are soluble in water, the rest in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colors.

4. *Hydrosulphuric acid* does not precipitate acid solutions; neutral solutions also it fails to precipitate, or precipitates them only very imperfectly.

5. *Sulphide of ammonium* throws down from neutral, and hydrosulphuric acid from alkaline solutions the whole of the metal as hydrated SULPHIDE OF MANGANESE (Mn S), in form of a light flesh-colored* precipitate, which acquires a dark-brown color in the air; this precipitate

* *If the quantity of the precipitate is only* trifling, the color appears yellowish white.

is insoluble in sulphide of ammonium and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids. The separation of the precipitate is materially promoted by addition of chloride of ammonium. From very dilute solutions the precipitate separates only after standing some time in a warm place. Oxalate of ammonia, tartrate of ammonia, and especially citrate of ammonia retard the precipitation, the latter salt also keeps up some of the manganese. In the presence of ammonia and sulphide of ammonium in large excess, the flesh-colored hydrated precipitate occasionally passes into the green anhydrous sulphide even in the cold, the change being greatly facilitated by boiling, and being hindered more or less by the presence of chloride of ammonium. Solutions containing much free ammonia must first be nearly neutralized with hydrochloric acid.

6. *Potassa*, *soda*, and *ammonia* produce whitish precipitates of HYDRATE OF PROTOXIDE OF MANGANESE ($MnO, HO$), which upon exposure to the air speedily acquire a brownish and finally a deep blackish-brown color, owing to the conversion of the hydrated protoxide into hydrated protosesquioxide by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate; but presence of chloride of ammonium prevents the precipitation by ammonia altogether, and that by potassa partly. Of already formed precipitates solution of chloride of ammonium redissolves only those parts which have not yet undergone peroxidation. The solution of the hydrated protoxide of manganese in chloride of ammonium is owing to the disposition of the salts of protoxide of manganese to form double salts with salts of ammonia. The ammoniacal solutions of these double salts turn brown in the air, and deposit dark-brown hydrate of protosesquioxide of manganese.

N.B. Non-volatile organic acids impede the precipitation of manganese by alkalies and alkaline carbonates. Sugar impedes the precipitation by alkalies, but not that by alkaline carbonates.

7. *Ferrocyanide of potassium* throws down FERROCYANIDE OF MANGANESE ($2Mn, Cfy$) as a reddish-white precipitate, soluble in hydrochloric acid.

8. *Ferricyanide of potassium* precipitates brown FERRICYANIDE OF MANGANESE ($3Mn, Cfdy$) insoluble in hydrochloric acid and ammonia.

9. If a few drops of a fluid containing protoxide of manganese, and free from chlorine, are sprinkled on *binoxide of lead* or *red-lead*, and nitric acid free from chlorine is added, the mixture boiled and allowed to settle, the fluid acquires a red color, from the formation of permanganic acid (HOPPE-SEYLER).

10. *Carbonate of baryta* does not precipitate protoxide of manganese from aqueous solutions of its salts upon digestion in the cold, with the exception of sulphate of protoxide of manganese.

11. If any compound of manganese, in a state of minute division, is fused with 2 or 3 parts of *carbonate of soda* on a platinum wire, or on a small strip of platinum foil (heated by directing the flame upon the lower surface), in the *outer* flame of the Bunsen or blowpipe, MANGANATE OF SODA ($NaO, MnO_3$) is formed, which makes the fused mass appear GREEN while hot, and of a BLUISH-GREEN tint after cooling, the bead at the same time losing its transparency. This reaction enables us to detect the smallest traces of manganese.

12. *Borax* and *phosphate of soda and ammonia* dissolve manganese

compounds in the outer gas or blowpipe flame to clear VIOLET-RED beads, which upon cooling acquire an AMETHYST-RED tint: they lose their color in the inner flame, owing to a reduction of the sesquioxide to protoxide. The borax bead appears black when containing a considerable portion of sesquioxide of manganese, but that formed by phosphate of soda and ammonia never loses its transparency. The latter loses its color in the inner flame of the blowpipe far more readily than the former.

## § 108.

### *c.* PROTOXIDE OF NICKEL (Ni O).

1. METALLIC NICKEL in the fused state is yellowish white, inclining to gray; it is bright, hard, malleable, difficultly fusible; it does not oxidize in the air at the common temperature, but it oxidizes slowly upon ignition; it is attracted by the magnet and may itself become magnetic. It slowly dissolves in hydrochloric acid and dilute sulphuric acid upon the application of heat, with evolution of hydrogen gas. It dissolves readily in nitric acid. The solutions contain protoxide of nickel.

2. HYDRATE OF PROTOXIDE OF NICKEL is light green, and remains unaltered in the air, but is converted by ignition to whiteness into green PROTOXIDE OF NICKEL. Both the protoxide and its hydrate are readily soluble in hydrochloric, nitric, and sulphuric acids. But the protoxide which crystallizes in octahedrons is insoluble in acids; it dissolves, however, in fusing bisulphate of potassa. SESQUIOXIDE OF NICKEL is black; it dissolves in hydrochloric acid to protochloride with evolution of chlorine. By gentle ignition of the nitrate, a protoxide containing a little sesquioxide of grayish-green color is obtained.

3. Most of the SALTS OF PROTOXIDE OF NICKEL are yellow in the anhydrous, green in the hydrated state; their solutions are light green. The soluble neutral salts slightly redden litmus-paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* does not precipitate solutions of salts with strong acids in presence of free acids; in the absence of free acid a small portion of the nickel gradually separates as black SULPHIDE OF NICKEL (Ni S).—Acetate of protoxide of nickel is not precipitated, or scarcely at all, in presence of free acetic acid. But in the absence of free acid the greater part of the nickel is thrown down by long-continued action of hydrosulphuric acid.

5. *Sulphide of ammonium* produces in neutral, and hydrosulphuric acid in alkaline solutions, a black precipitate of hydrated SULPHIDE OF NICKEL (Ni S), which is not altogether insoluble in sulphide of ammonium, especially if the latter contain free ammonia; the fluid from which the precipitate has been thrown down exhibits therefore usually a brownish color. The presence of chloride of ammonium, and still more of acetate of ammonia, considerably promotes the precipitation. Sulphide of nickel dissolves scarcely at all in acetic acid, with great difficulty in hydrochloric acid, but readily in nitro-hydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce a light green precipitate of HYDRATE OF PROTOXIDE OF NICKEL (Ni O, H O), which is insoluble in an excess of the precipitants, and unalterable in the air, and on boiling (even in the presence of alcohol). Carbonate of ammonia dissolves this precipi-

tate, when filtered and washed, to a greenish-blue fluid, from which potassa or soda reprecipitates the nickel as an apple-green hydrate of protoxide.

7. *Ammonia* added in small quantity produces a trifling greenish turbidity; upon further addition of the reagent this redissolves readily to a blue fluid containing a compound of PROTOXIDE OF NICKEL AND AMMONIA. Potassa and soda precipitate from this solution hydrate of protoxide of nickel. Solutions containing salts of ammonia or free acid are not rendered turbid by ammonia.

N.B. The presence of non-volatile organic acids, and of sugar, impedes the precipitation by alkalies.

8. *Ferrocyanide of potassium* precipitates greenish-white FERROCYANIDE OF NICKEL (2 Ni, Cfy), which is insoluble in hydrochloric acid.

9. *Ferricyanide of potassium* precipitates yellowish-brown FERRICYANIDE OF NICKEL (3 Ni, Cfdy), which is insoluble in hydrochloric acid.

10. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL (Ni Cy), which redissolves readily in an excess of the precipitant as a double cyanide of nickel and potassium (Ni Cy, K Cy); the solution is brownish-yellow, and does not acquire a darker color on exposure to the air. If sulphuric acid or hydrochloric acid is added to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel reprecipitated. From more highly dilute solutions the cyanide of nickel separates only after some time; it is very difficultly soluble in an excess of the precipitating acids in the cold, but more readily upon boiling. If the solution of the double cyanide is rendered alkaline by solution of soda, being also kept so by a further addition of soda if necessary, and chlorine gas is passed into it without warming, the whole of the nickel gradually separates as black hydrate of sesquioxide.

11. On adding to solutions which are not too dilute and which have been rendered alkaline by ammonia, a solution of sulphocarbonate of potassium,* a deep brownish-red fluid is obtained which is barely translucent, and appears almost black by reflected light. If the solution of nickel is extremely dilute, the addition of the reagent will produce a delicate pink color (C. D. BRAUN). The occurrence of this color in highly dilute solutions is characteristic of nickel.

12. *Carbonate of baryta*, on digestion in the cold with solutions, does not precipitate nickel, unless sulphuric acid is present.

13. *Nitrite of potassa* with acetic acid does not throw down the nickel, even from concentrated solutions. In the presence of lime, baryta, or strontia, however, a yellow crystalline nitrite of protoxide of nickel and the alkaline earth is precipitated from not too dilute solutions. The precipitate is difficultly soluble in cold water, more readily in hot water to a green fluid (KÜNZEL, O. L. ERDMANN).

14. *Borax* and *microcosmic salt* dissolve compounds of protoxide of nickel in the outer flame to clear beads. The borax bead is violet while hot, reddish-brown when cold; the microcosmic bead is reddish or

* Prepared by taking a solution of hydrate of potassa containing about 5 per cent., *saturating* one-half with hydrosulphuric acid, adding the other half and then $\frac{1}{10}$ of the *volume of* bisulphide of carbon, digesting at a gentle heat, and finally separating the *dark orange*-red fluid from the undissolved bisulphide of carbon. The solution must *be kept in* a well-closed bottle.

brownish-red while hot, yellow or reddish-yellow when cold. In the inner flame the microcosmic bead remains unaltered, but the borax bead becomes gray and cloudy from reduced metal. On continued heating the particles of nickel collect together without fusing, and the bead loses its color.

15. By the reduction in the *stick of charcoal*, according to p. 24, the compounds of nickel yield after trituration white, shining, ductile spangles, which will be deposited on the point of a magnetic knife in the form of a brush. With nitric acid they give a green solution, which can be further examined.

## § 109.

### *d.* Protoxide of Cobalt (Co O).

1. Metallic cobalt in the fused state is steel-gray, pretty hard, malleable, difficultly fusible, and magnetic; susceptible of polish; it does not oxidize in the air at the common temperature, but it oxidizes at a red heat; with acids it behaves like nickel. The solutions contain protoxide of cobalt.

2. Protoxide of cobalt is light brown, its hydrate a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids. Sesquioxide of cobalt is black; it dissolves in hydrochloric acid to protochloride, with evolution of chlorine.

3. The salts of protoxide of cobalt containing water of crystallization are red, the anhydrous salts mostly blue. The moderately concentrated solutions appear of a light red color, which they retain even though considerably diluted. The soluble neutral salts redden litmus slightly, and are decomposed at a red heat; sulphate of protoxide of cobalt alone can bear a moderate red heat without suffering decomposition. When a solution of chloride of cobalt is evaporated, the light red color changes towards the end of the operation to blue; addition of water restores the red color.

4. *Hydrosulphuric acid* does not precipitate solutions of salts with strong acids, if they contain free acid; from neutral solutions it gradually precipitates part of the cobalt as black sulphide of cobalt (Co S). Acetate of protoxide of cobalt is not precipitated, or to a very slight extent, in presence of free acetic acid. But in the absence of free acid it is completely precipitated, or almost completely.

5. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions, the whole of the metal as black hydrated sulphide of cobalt (Co S). Chloride of ammonium promotes the precipitation most materially. Sulphide of cobalt is insoluble in alkalies and sulphide of ammonium, scarcely soluble in acetic acid, very difficultly soluble in hydrochloric acid, but readily so in nitro-hydrochloric acid, upon application of heat.

6. *Potassa* and *soda* produce blue precipitates of basic salts of cobalt, insoluble in excess of the precipitants, which turn green upon exposure to the air, owing to the absorption of oxygen. Upon boiling they are converted into pale red hydrate of protoxide of cobalt, which contains alkali, and generally appears rather discolored from sesquioxide formed in the process. If before boiling alcohol is added, *the precipitate is rapidly converted* into dark brown hydrate of the *sesquioxide. Neutral carbonate* of ammonia dissolves the washed pre-

cipitates of basic salt or hydrated protoxide completely to intensely violet-red fluids, in which a somewhat larger proportion of potassa or soda produces a blue precipitate, the fluid still retaining its violet color.

7. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish fluid, which turns brownish-red on exposure to the air, from which potassa or soda throws down a portion of the cobalt as blue basic salt. Ammonia produces no precipitate in solutions containing ammonia salts or a free acid.

N.B. The presence of non-volatile organic acids or sugar checks the precipitation by alkalies.

8. *Ferrocyanide of potassium* throws down green FERROCYANIDE OF COBALT (2 Co, Cfy), insoluble in hydrochloric acid.

9. *Ferricyanide of potassium* throws down brownish-red FERRICYANIDE OF COBALT (3 Co, Cfdy), insoluble in hydrochloric acid.

10. Addition of *cyanide of potassium* gives rise to the formation of a brownish-white precipitate of PROTOCYANIDE OF COBALT (Co Cy), which dissolves readily in excess of the precipitant as a double cyanide of cobalt and potassium. Acids precipitate from this solution cyanide of cobalt. But if the solution is boiled with cyanide of potassium in excess, in presence of free hydrocyanic acid (liberated by addition of one or two drops of hydrochloric acid), or if the solution is mixed with potassa or soda and chlorine is passed through it without warming, the double cyanide is converted into cobalticyanide of potassium ($K_3, Co_2 Cy_6 = K_3 Ccdy$), and acids will now produce no precipitate (essential difference between cobalt and nickel). Nitrite of potassa and acetic acid added to the unaltered solution of the double cyanide produces a blood-red color in consequence of the formation of nitrocyanide of cobalt and potassium; when the liquid is very dilute the color is merely orange red. Solution of soda added to the double cyanide occasions a brown color when the fluid is shaken, oxygen being absorbed (essential differences between cobalt and nickel, C. D. BRAUN).

11. *Sulphocarbonate of potassium*, added to solutions which have been rendered alkaline by ammonia, produces a dark brown, almost black color; if the solution is very dilute a pale straw color.

12. Addition of tartaric or citric acid, then of ammonia in excess, and lastly of *ferricyanide of potassium*, produces a deep yellowish-red color; with extremely dilute solutions a rose color (SKEY). This is a very delicate reaction, well suited for the detection of cobalt in the presence of nickel.

13. *Carbonate of baryta* behaves in the same way as to solutions of nickel.

14. If *nitrite of potassa* is added in not too small proportion to a solution of protoxide of cobalt, then acetic acid to strongly acid reaction, and the mixture put in a moderately warm place, all the cobalt separates, from concentrated solutions very soon, from dilute solutions after some time, in the form of a crystalline precipitate of a beautiful yellow color (FISCHER, STROMEYER). STROMEYER considers this precipitate to be a NITRITE OF SESQUIOXIDE OF COBALT AND POTASSA ($Co_2O_3, 3 K O, 5 N O_3, 2 H O$), and its formation may be then accounted for in the following way: $2 (Co O, S O_3) + 6 (K O, N O_3) + H O, \bar{A} + H O = K O, \bar{A} + 2 (K O, S O_3) + Co_2O_3, 3 K O, 5 N O_3, 2 H O + N O_3$.*

* C. D. BRAUN (Zeitschr. f. anal. Chem., 7, 335), on the contrary, considers the precipitate to be a mixture of various compounds.

The precipitate is very perceptibly soluble in water, scarcely soluble in concentrated solutions of potassa salts and in alcohol, insoluble in presence of nitrite of potassa. When boiled with water it dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down hydrate of protoxide of cobalt. This excellent reaction serves well to distinguish and separate cobalt from nickel.

15. *Borax* dissolves compounds of cobalt in the inner and outer flame to clear beads of a magnificent blue color, which appear violet by candlelight, and are almost black in the presence of a large quantity of cobalt. This test is as delicate as it is characteristic. Phosphate of soda and ammonia gives the same reaction, but it is less delicate.

16. In the reduction with the *stick of charcoal*, according to p. 24, compounds of cobalt behave in the same way as compounds of nickel. The solution with nitric acid is red.

## § 110.

### *e.* Protoxide of Iron (Fe O).

1. Metallic iron in the pure state has a light whitish-gray color (iron containing carbon is more or less gray); the metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture a coating of rust (hydrate of sesquioxide of iron) forms on its surface: upon ignition in the air a coating of black protosesquioxide. Hydrochloric acid and dilute sulphuric acid dissolve iron, with evolution of hydrogen gas; if the iron contains carbide, the hydrogen is mixed with carbide of hydrogen. The solutions contain protoxide. Dilute nitric acid dissolves iron in the cold to nitrate of protoxide, with evolution of nitrous oxide; at a high temperature to nitrate of sesquioxide, with evolution of nitric oxide; if the iron contains carbide, some carbonic acid is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies; when graphite is present, it also is left behind.

2. Protoxide of iron is black; its hydrate is white, and in the moist state absorbs oxygen and speedily acquires a grayish-green, and ultimately a brownish-red color. Both the protoxide and its hydrate are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. The salts of protoxide of iron have in the anhydrous state a white, in the hydrated state a greenish color; their solutions only look greenish when concentrated. The latter absorb oxygen when exposed to the air, and are converted into salts of the protosesquioxide, with precipitation of basic salts of sesquioxide. Chlorine or nitric acid converts them by boiling into salts of sesquioxide. The soluble neutral salts redden litmus-paper, and are decomposed at a red heat.

4. Solutions of salts of protoxide of iron made acid by strong acids are not precipitated by *hydrosulphuric acid*; nor are neutral solutions nor solutions acidified with weak acids precipitated by this reagent, or at the most but very incompletely.

5. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions, the whole of the metal as black hydrated protosulphide of iron (Fe S), which is insoluble in alka-

lies and sulphides of the alkali metals, but dissolves readily in hydrochloric and nitric acids: this black precipitate turns reddish-brown in the air by oxidation. To highly dilute solutions sulphide of ammonium imparts a green color, and it is only after some time that the protosulphide of iron separates as a black precipitate. Chloride of ammonium promotes the precipitation most materially.

6. *Potassa* and *ammonia* produce a precipitate of HYDRATE OF PROTOXIDE OF IRON (Fe O, H O), which in the first moment looks almost white, but acquires after a very short time a dirty green, and ultimately a reddish-brown color, owing to absorption of oxygen from the air. Presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If alkaline solutions of protoxide of iron thus obtained by the agency of salts of ammonia are exposed to the air, hydrate of protosesquioxide of iron and hydrate of sesquioxide of iron precipitate. Non-volatile organic acids, sugar, &c., check the precipitation by alkalies.

7. *Ferrocyanide of potassium* produces a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON ($K, Fe_2, Cfy_2$), which, by absorption of oxygen from the air, speedily acquires a blue color. Nitric acid or chlorine converts it immediately into Prussian blue, $3\,(K, Fe_2, Cfy_2) + 4\,Cl = 3\,K\,Cl + Fe\,Cl + 2\,(Fe_4 Cfy_3)$.

8. *Ferricyanide of potassium* produces a magnificently blue precipitate of FERRICYANIDE OF IRON ($Fe_2$ Cfdy). This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions the reagent produces simply a deep blue-green coloration.

9. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron free from sesquioxide.

10. *Carbonate of baryta* does not precipitate solutions of protoxide of iron in the cold, with the exception of the sulphate.

11. *Borax* dissolves protoxide of iron compounds in the oxidizing flame, giving beads varying in color from yellow to dark red; when cold the beads vary from colorless to dark yellow. In the inner flame the beads change to bottle-green, owing to the reduction of the newly-formed sesquioxide to protosesquioxide. Phosphate of soda and ammonia shows a similar reaction; the beads produced with this reagent lose their color upon cooling still more completely than those produced with borax; the signs of the ensuing reduction in the reducing flame are also less marked.

12. When reduced in the *stick of charcoal* (p. 24), compounds of protoxide of iron give a dull black powder, which is attracted by a magnetic knife. The reduced metal, when dissolved in a few drops of aqua regia, gives a yellow fluid, which can be further tested according to § 111.

## § 111.

### *f.* SESQUIOXIDE OF IRON ($Fe_2 O_3$).

1. The native crystallized SESQUIOXIDE OF IRON is steel-gray; the native as well as the artificially prepared sesquioxide of iron gives upon trituration a brownish-red powder; the color of hydrate of sesquioxide of iron is more inclined to reddish-brown. Both the sesquioxide and *its hydrate dissolve* in hydrochloric, nitric, and sulphuric acids; the

hydrate dissolves readily in these acids, but the anhydrous sesquioxide dissolves with greater difficulty, and completely only after long exposure to heat. PROTOSESQUIOXIDE OF IRON ($FeO, Fe_2O_3$) is black; it dissolves in hydrochloric acid to protochloride and sesquichloride, in aqua regia to sesquichloride.

2. The neutral anhydrous SALTS OF SESQUIOXIDE OF IRON are nearly white; the basic salts are yellow or reddish-brown. The color of the solutions is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble neutral salts redden litmus-paper, and are decomposed by heat.

3. *Hydrosulphuric acid* produces in solutions made acid by stronger acids a milky white turbidity, proceeding from separated SULPHUR; the salt of the sesquioxide being at the same time converted into salt of the protoxide: $Fe_2O_3, 3SO_3 + HS = 2(FeO\,SO_3) + HO, SO_3 + S$. If solution of hydrosulphuric acid is rapidly added to neutral solutions, a transient blackening of the fluid also occurs. From solution of neutral acetate of sesquioxide of iron hydrosulphuric acid throws down the greater part of the iron; but in presence of a sufficient quantity of free acetic acid sulphur alone separates.

4. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions, the whole of the metal as black hydrated PROTOSULPHIDE OF IRON (FeS) mixed with sulphur; $Fe_2Cl_3 + 3NH_4S = 3NH_4Cl + 2FeS + S$. In very dilute solutions the reagent produces only a blackish-green coloration. The minutely divided protosulphide of iron subsides in such cases only after long standing. Chloride of ammonium most materially promotes the precipitation. Protosulphide of iron, as already stated (§ 110, 5), is insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric and nitric acids.

5. *Potassa* and *ammonia* produce bulky reddish-brown precipitates of HYDRATE OF SESQUIOXIDE OF IRON ($Fe_2O_3, 2HO$), which are insoluble in an excess of the precipitant as well as in salts of ammonia. Non-volatile organic acids and sugar, when present in sufficient quantity, entirely prevent the precipitation.

6. *Ferrocyanide of potassium* produces even in highly dilute solutions a magnificently blue precipitate of FERROCYANIDE OF IRON, or Prussian blue ($Fe_4Cfy_3$): $2(Fe_2Cl_3) + 3(Cfy, 2K) = 6KCl + Fe_4Cfy_3$. This precipitate is insoluble in hydrochloric acid, but is decomposed by potassa, with separation of hydrate of sesquioxide of iron.

7. *Ferricyanide of potassium* deepens the color of solutions of sesquioxide of iron to reddish-brown; but it fails to produce a precipitate.

8. *Sulphocyanide of potassium* imparts to acid solutions a most intense blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON. This color does not disappear on the addition of a little alcohol and warming (difference from the analogous reaction of hyponitric acid, § 158). Solutions of sesquioxide of iron, containing acetate of soda (which consequently are more or less red from acetate of sesquioxide of iron), do not show the blood-red color of the sulphocyanide till after the addition of much hydrochloric acid. The same remark applies to solutions containing an alkaline fluoride or an oxalate. This test will indicate the presence of iron even in fluids, which are so highly dilute that every other reagent fails to produce in them the slightest visible alteration. The red coloration may in

such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may also be increased by shaking gently with ether after the addition of hydrochloric acid, and of excess of sulphocyanide of potassium solution freshly prepared from the crystals. The sulphocyanide of iron dissolves in the ether, and the layer of the latter acquires a more or less red color.

9. *Carbonate of baryta* precipitates even in the cold all the iron as HYDRATE OF SESQUIOXIDE MIXED WITH A BASIC SALT.

10. The reactions before the *blowpipe* are the same as with the protoxide.

## § 112.

*Recapitulation and remarks.*—On observing the reactions of the several oxides of the fourth group with solution of potassa, it would appear that the separation of the oxide of zinc, which is soluble in an excess of this reagent, might be readily effected by its means; but in the actual experiment we find that rather notable quantities of oxide of zinc are thrown down with the sesquioxide of iron, protoxide of cobalt, &c. To such an extent indeed that it is often impossible to demonstrate the presence of oxide of zinc in the alkaline filtrate. This method would be entirely inadmissible in the presence of sesquioxide of chromium, as solutions of the latter and of oxide of zinc in potassa mutually precipitate each other.

Again, the reactions of the different oxides with chloride of ammonium and an access of ammonia would lead to the conclusion that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also if applied to the mixed oxides is inaccurate, since greater or smaller portions of the other oxides will always precipitate along with the sesquioxide of iron; and it may therefore happen that small quantities of cobalt, manganese, &c., altogether escape detection in this process.

It is far safer therefore to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta, as in that case the iron is precipitated free from oxide of zinc and protoxide of manganese, and, if chloride of ammonium is added previously to the addition of the carbonate of baryta, almost entirely free also from protoxide of nickel and protoxide of cobalt. Instead of using the carbonate of baryta for the separation of sesquioxide of iron, we may proceed as follows: nearly neutralize any excess of acid with carbonate of soda, add acetate of soda and boil; or mix the sufficiently diluted solution with a rather large quantity of chloride of ammonium, cautiously add carbonate of ammonia till the fluid commences to become cloudy, the reaction still remaining acid, and then boil. In each of these two last methods the basic salt of sesquioxide of iron must be filtered off hot.

Protoxide of manganese may conveniently be separated from the protoxides of cobalt and nickel, as well as from oxide of zinc, by treating the washed precipitated sulphides with moderately dilute acetic acid, which dissolves the sulphide of manganese, leaving the other sulphides *undissolved*. If the acetic acid solution is now evaporated and mixed *with solution* of potassa, the least trace of a precipitate will be sufficient

to recognise the manganese before the blowpipe with carbonate of soda. If the sulphides left undissolved by acetic acid are now treated, after washing, with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled, and strongly concentrated to expel the hydrosulphuric acid, and afterwards treated with solution of potassa or soda in excess without warming, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

On drying the filter containing the sulphides of nickel and cobalt, incinerating it in a small porcelain dish, and testing a portion of the residue with borax in the inner blowpipe flame, the cobalt may generally be detected with certainty even in the presence of nickel. The detection of nickel in presence of cobalt is not quite so simple a matter. It is best done by warming the rest of the residue with a little aqua regia, diluting, filtering, evaporating the solution to a small bulk, mixing with a sufficiency of nitrite of potassa, adding acetic acid to strongly acid reaction, and setting aside in a moderately warm place for at least twelve hours. The cobalt then separates as nitrite of sesquioxide of cobalt and potassa; the nickel may be precipitated from the filtrate by solution of soda, and, to prevent mistakes, tested before the blowpipe, or according to § 108, 11, after considerable dilution. For the detection of small quantities of nickel in presence of large quantities of cobalt, it is still better to use the solution of the cyanides in cyanide of potassium mixed with solution of soda. In this solution the presence of cobalt will be shown by a dark color on exposure to the air, the presence of nickel by the separation of black sesquioxide on treatment with chlorine (§ 108, 10, and § 109, 10).

In practical analysis we generally separate the whole of the oxides of the fourth group as sulphides by precipitation with sulphide of ammonium. It is therefore in most cases still more convenient to separate nickel and cobalt, or at least the far larger portion of these two metals, at the outset. To this end the moist precipitate of the sulphides is treated with water and some hydrochloric acid, with active stirring, but without application of heat. Nearly the whole of the sulphide of nickel and sulphide of cobalt is left behind undissolved, whilst all the other sulphides are dissolved. The undissolved residue of sulphide of cobalt and sulphide of nickel is filtered and washed, and treated as directed above. By boiling the filtrate with nitric acid the iron is converted from the state of protoxide, as it existed in the solution of the sulphide, into that of sesquioxide. After the free acid has been nearly neutralized by carbonate of soda, the iron may be thrown down as basic salt either by carbonate of baryta in the cold, or by acetate of soda and boiling. Manganese and zinc alone remain in the filtrate; these metals are then also precipitated with sulphide of ammonium and some chloride of ammonium, the precipitate is filtered and washed, and the two metals are finally separated from each other by acetic acid as directed above, or, after removal of the baryta by sulphuric acid and great concentration, by solution of potassa or soda. The trifling quantities of cobalt and nickel, dissolved on the first treatment of the sulphide precipitate with dilute hydrochloric acid, remain with the sulphide of zinc in the separation of the latter from the sulphide of manganese by acetic acid—or with the protoxide of manganese if the separation is effected by solution of potassa or soda. The sulphide of zinc may be extracted from

such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may also be increased by shaking gently with ether after the addition of hydrochloric acid, and of excess of sulphocyanide of potassium solution freshly prepared from the crystals. The sulphocyanide of iron dissolves in the ether, and the layer of the latter acquires a more or less red color.

9. *Carbonate of baryta* precipitates even in the cold all the iron as HYDRATE OF SESQUIOXIDE MIXED WITH A BASIC SALT.

10. The reactions before the *blowpipe* are the same as with the protoxide.

## § 112.

*Recapitulation and remarks.*—On observing the reactions of the several oxides of the fourth group with solution of potassa, it would appear that the separation of the oxide of zinc, which is soluble in an excess of this reagent, might be readily effected by its means; but in the actual experiment we find that rather notable quantities of oxide of zinc are thrown down with the sesquioxide of iron, protoxide of cobalt, &c. To such an extent indeed that it is often impossible to demonstrate the presence of oxide of zinc in the alkaline filtrate. This method would be entirely inadmissible in the presence of sesquioxide of chromium, as solutions of the latter and of oxide of zinc in potassa mutually precipitate each other.

Again, the reactions of the different oxides with chloride of ammonium and an access of ammonia would lead to the conclusion that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also if applied to the mixed oxides is inaccurate, since greater or smaller portions of the other oxides will always precipitate along with the sesquioxide of iron; and it may therefore happen that small quantities of cobalt, manganese, &c., altogether escape detection in this process.

It is far safer therefore to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta, as in that case the iron is precipitated free from oxide of zinc and protoxide of manganese, and, if chloride of ammonium is added previously to the addition of the carbonate of baryta, almost entirely free also from protoxide of nickel and protoxide of cobalt. Instead of using the carbonate of baryta for the separation of sesquioxide of iron, we may proceed as follows: nearly neutralize any excess of acid with carbonate of soda, add acetate of soda and boil; or mix the sufficiently diluted solution with a rather large quantity of chloride of ammonium, cautiously add carbonate of ammonia till the fluid commences to become cloudy, the reaction still remaining acid, and then boil. In each of these two last methods the basic salt of sesquioxide of iron must be filtered off hot.

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to recognise the manganese before the blowpipe with carbonate of soda. If the sulphides left undissolved by acetic acid are now treated, after washing, with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled, and strongly concentrated to expel the hydrosulphuric acid, and afterwards treated with solution of potassa or soda in excess without warming, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

On drying the filter containing the sulphides of nickel and cobalt, incinerating it in a small porcelain dish, and testing a portion of the residue with borax in the inner blowpipe flame, the cobalt may generally be detected with certainty even in the presence of nickel. The detection of nickel in presence of cobalt is not quite so simple a matter. It is best done by warming the rest of the residue with a little aqua regia, diluting, filtering, evaporating the solution to a small bulk, mixing with a sufficiency of nitrite of potassa, adding acetic acid to strongly acid reaction, and setting aside in a moderately warm place for at least twelve hours. The cobalt then separates as nitrite of sesquioxide of cobalt and potassa; the nickel may be precipitated from the filtrate by solution of soda, and, to prevent mistakes, tested before the blowpipe, or according to § 108, 11, after considerable dilution. For the detection of small quantities of nickel in presence of large quantities of cobalt, it is still better to use the solution of the cyanides in cyanide of potassium mixed with solution of soda. In this solution the presence of cobalt will be shown by a dark color on exposure to the air, the presence of nickel by the separation of black sesquioxide on treatment with chlorine (§ 108, 10, and § 109, 10).

In practical analysis we generally separate the whole of the oxides of the fourth group as sulphides by precipitation with sulphide of ammonium. It is therefore in most cases still more convenient to separate nickel and cobalt, or at least the far larger portion of these two metals, at the outset. To this end the moist precipitate of the sulphides is treated with water and some hydrochloric acid, with active stirring, but without application of heat. Nearly the whole of the sulphide of nickel and sulphide of cobalt is left behind undissolved, whilst all the other sulphides are dissolved. The undissolved residue of sulphide of cobalt and sulphide of nickel is filtered and washed, and treated as directed above. By boiling the filtrate with nitric acid the iron is converted from the state of protoxide, as it existed in the solution of the sulphide, into that of sesquioxide. After the free acid has been nearly neutralized by carbonate of soda, the iron may be thrown down as basic salt either by carbonate of baryta in the cold, or by acetate of soda and boiling. Manganese and zinc alone remain in the filtrate; these metals are then also precipitated with sulphide of ammonium and some chloride of ammonium, the precipitate is filtered and washed, and the two metals are finally separated from each other by acetic acid as directed above, or, after removal of the baryta by sulphuric acid and great concentration, by solution of potassa or soda. The trifling quantities of cobalt and nickel, dissolved on the first treatment of the sulphide precipitate with dilute hydrochloric acid, remain with the sulphide of zinc in the separation of the latter from the sulphide of manganese by acetic acid—or with the protoxide of manganese if the separation is effected by solution of potassa or soda. The sulphide of zinc may be extracted from

such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may also be increased by shaking gently with ether after the addition of hydrochloric acid, and of excess of sulphocyanide of potassium solution freshly prepared from the crystals. The sulphocyanide of iron dissolves in the ether, and the layer of the latter acquires a more or less red color.

9. *Carbonate of baryta* precipitates even in the cold all the iron as HYDRATE OF SESQUIOXIDE MIXED WITH A BASIC SALT.

10. The reactions before the *blowpipe* are the same as with the protoxide.

## § 112.

*Recapitulation and remarks.*—On observing the reactions of the several oxides of the fourth group with solution of potassa, it would appear that the separation of the oxide of zinc, which is soluble in an excess of this reagent, might be readily effected by its means; but in the actual experiment we find that rather notable quantities of oxide of zinc are thrown down with the sesquioxide of iron, protoxide of cobalt, &c. To such an extent indeed that it is often impossible to demonstrate the presence of oxide of zinc in the alkaline filtrate. This method would be entirely inadmissible in the presence of sesquioxide of chromium, as solutions of the latter and of oxide of zinc in potassa mutually precipitate each other.

Again, the reactions of the different oxides with chloride of ammonium and an access of ammonia would lead to the conclusion that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also if applied to the mixed oxides is inaccurate, since greater or smaller portions of the other oxides will always precipitate along with the sesquioxide of iron; and it may therefore happen that small quantities of cobalt, manganese, &c., altogether escape detection in this process.

It is far safer therefore to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta, as in that case the iron is precipitated free from oxide of zinc and protoxide of manganese, and, if chloride of ammonium is added previously to the addition of the carbonate of baryta, almost entirely free also from protoxide of nickel and protoxide of cobalt. Instead of using the carbonate of baryta for the separation of sesquioxide of iron, we may proceed as follows: nearly neutralize any excess of acid with carbonate of soda, add acetate of soda and boil; or mix the sufficiently diluted solution with a rather large quantity of chloride of ammonium, cautiously add carbonate of ammonia till the fluid commences to become cloudy, the reaction still remaining acid, and then boil. In each of these two last methods the basic salt of sesquioxide of iron must be filtered off hot.

Protoxide of manganese may conveniently be separated from the protoxides of cobalt and nickel, as well as from oxide of zinc, by treating the washed precipitated sulphides with moderately dilute acetic acid, which dissolves the sulphide of manganese, leaving the other sulphides undissolved. If the acetic acid solution is now evaporated and mixed with solution of potassa, the least trace of a precipitate will be sufficient

to recognise the manganese before the blowpipe with carbonate of soda. If the sulphides left undissolved by acetic acid are now treated, after washing, with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled, and strongly concentrated to expel the hydrosulphuric acid, and afterwards treated with solution of potassa or soda in excess without warming, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

On drying the filter containing the sulphides of nickel and cobalt, incinerating it in a small porcelain dish, and testing a portion of the residue with borax in the inner blowpipe flame, the cobalt may generally be detected with certainty even in the presence of nickel. The detection of nickel in presence of cobalt is not quite so simple a matter. It is best done by warming the rest of the residue with a little aqua regia, diluting, filtering, evaporating the solution to a small bulk, mixing with a sufficiency of nitrite of potassa, adding acetic acid to strongly acid reaction, and setting aside in a moderately warm place for at least twelve hours. The cobalt then separates as nitrite of sesquioxide of cobalt and potassa; the nickel may be precipitated from the filtrate by solution of soda, and, to prevent mistakes, tested before the blowpipe, or according to § 108, 11, after considerable dilution. For the detection of small quantities of nickel in presence of large quantities of cobalt, it is still better to use the solution of the cyanides in cyanide of potassium mixed with solution of soda. In this solution the presence of cobalt will be shown by a dark color on exposure to the air, the presence of nickel by the separation of black sesquioxide on treatment with chlorine (§ 108, 10, and § 109, 10).

In practical analysis we generally separate the whole of the oxides of the fourth group as sulphides by precipitation with sulphide of ammonium. It is therefore in most cases still more convenient to separate nickel and cobalt, or at least the far larger portion of these two metals, at the outset. To this end the moist precipitate of the sulphides is treated with water and some hydrochloric acid, with active stirring, but without application of heat. Nearly the whole of the sulphide of nickel and sulphide of cobalt is left behind undissolved, whilst all the other sulphides are dissolved. The undissolved residue of sulphide of cobalt and sulphide of nickel is filtered and washed, and treated as directed above. By boiling the filtrate with nitric acid the iron is converted from the state of protoxide, as it existed in the solution of the sulphide, into that of sesquioxide. After the free acid has been nearly neutralized by carbonate of soda, the iron may be thrown down as basic salt either by carbonate of baryta in the cold, or by acetate of soda and boiling. Manganese and zinc alone remain in the filtrate; these metals are then also precipitated with sulphide of ammonium and some chloride of ammonium, the precipitate is filtered and washed, and the two metals are finally separated from each other by acetic acid as directed above, or, after removal of the baryta by sulphuric acid and great concentration, by solution of potassa or soda. The trifling quantities of cobalt and nickel, dissolved on the first treatment of the sulphide precipitate with dilute hydrochloric acid, remain with the sulphide of zinc in the separation of the latter from the sulphide of manganese by acetic acid—or with the protoxide of manganese if the separation is effected by solution of potassa or soda. The sulphide of zinc may be extracted from

fusion in the air. Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. OXIDE OF SILVER is a grayish-brown powder; it is not altogether insoluble in water, and dissolves readily in dilute nitric acid. It forms no hydrate. It is decomposed by heat into metallic silver and oxygen gas. The black suboxide of silver ($Ag_2O$) and the binoxide are likewise decomposed by heat into metallic silver and oxygen.

3. The SALTS OF OXIDE OF SILVER are non-volatile and colorless; many of them acquire a black tint upon exposure to light. The soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* precipitate black SULPHIDE OF SILVER (Ag S) which is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassa* and *soda* precipitate OXIDE OF SILVER in the form of a grayish-brown powder, which is insoluble in an excess of the precipitants, but dissolves readily in ammonia.

6. *Ammonia*, if added in very small quantity to neutral solutions, throws down the OXIDE as a brown precipitate, which readily redissolves in an excess of ammonia. Acid solutions are not precipitated.

7. *Hydrochloric acid* and *soluble metallic chlorides* produce a white curdy precipitate of CHLORIDE OF SILVER (Ag Cl). In very dilute solutions these reagents impart at first simply a bluish-white opalescent appearance to the fluid; but after long standing in a warm place the chloride of silver collects at the bottom of the vessel. By the action of light the white chloride of silver loses chlorine, first acquiring a violet tint, and ultimately turning black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is again separated by acids. Concentrated hydrochloric acid and concentrated solutions of chlorides of the alkali metals dissolve chloride of silver to a very perceptible amount, more particularly upon application of heat; but the dissolved chloride separates again upon dilution. Upon exposure to heat chloride of silver fuses without decomposition, giving upon cooling a translucent horny mass.

8. If compounds of silver mixed with *carbonate of soda* are exposed on a charcoal support to the *inner flame of the blowpipe*, white brilliant malleable metallic globules are obtained, with or without a slight dark red incrustation of the charcoal. The metal is also readily reduced in the *stick of charcoal* (p. 24).

## § 116.

### *b.* SUBOXIDE OF MERCURY ($Hg_2O$).

1. METALLIC MERCURY is grayish-white, lustrous, fluid at the common temperature; it solidifies at $-39°$, and boils at 360°. It is insoluble in hydrochloric acid; in dilute cold nitric acid it dissolves to nitrate of suboxide, in concentrated hot nitric acid to nitrate of oxide of mercury.

2. SUBOXIDE OF MERCURY is a black powder, readily soluble in,

nitric acid. It is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

3. The SALTS OF SUBOXIDE OF MERCURY volatilize upon ignition; most of them suffer decomposition in this process. Subchloride and subbromide of mercury volatilize unaltered. Most of the salts of suboxide of mercury are colorless. The soluble salts in the neutral state redden litmus-paper. Nitrate of suboxide of mercury is decomposed by addition of much water into a light yellow insoluble basic and a soluble acid salt.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce black precipitates, which are insoluble in dilute acids, sulphide of ammonium, and cyanide of potassium. The precipitates consist of SULPHIDE OF MERCURY MIXED WITH MERCURY. Monosulphide of sodium, in presence of some caustic soda, dissolves this precipitate with separation of metallic mercury; bisulphide of sodium dissolves it without separation of metallic mercury; the solutions contain sulphide of mercury. The precipitate gives up mercury to boiling concentrated nitric acid with formation of a white double compound, namely, $HgO, NO_5 + 2HgS$. The precipitate is readily dissolved by aqua regia.

5. *Potassa*, *soda*, and *ammonia* produce black precipitates, which are insoluble in an excess of the precipitants. The precipitates produced by the fixed alkalies consist of SUBOXIDE OF MERCURY; whilst those produced by ammonia consist of BASIC SALTS CONTAINING AMMONIA OR AMIDOGEN.

6. *Hydrochloric acid* and *soluble metallic chlorides* precipitate SUBCHLORIDE OF MERCURY ($Hg_2Cl$) as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves however, although very difficultly and slowly, upon long-continued boiling with these acids, being resolved by hydrochloric acid into chloride of mercury and metallic mercury, which separates; and converted by nitric acid into chloride of mercury and nitrate of oxide of mercury. Nitrohydrochloric acid and chlorine water dissolve the subchloride of mercury readily, converting it into chloride. Ammonia and potassa decompose the subchloride of mercury, separating from it, the former a compound of subamide of mercury with subchloride of mercury ($Hg_2NH_2, Hg_2Cl$), the latter suboxide of mercury.

7. If a drop of a neutral or slightly acid solution is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards, on being gently rubbed with cloth, paper, &c., appear white and lustrous like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the silvering.

8. *Protochloride of tin* produces a gray precipitate of METALLIC MERCURY, which may be united into globules by boiling the metallic deposit, after decanting the fluid, with hydrochloric acid, to which a little protochloride of tin may also be added.

9. If an intimate mixture of an anhydrous compound of mercury with anhydrous *carbonate of soda* is introduced into a sealed glass tube, and covered with a layer of carbonate of soda, and the tube is then strongly heated, the mercurial compound invariably undergoes decomposition, and METALLIC MERCURY separates, forming a coat of gray sublimate above the heated part of the tube. By means of a lens the

sublimate will be seen to consist of globules of metal. Larger globules may be obtained by rubbing the sublimate with a glass rod.

## § 117.

### *c.* Oxide of Lead (Pb O).

1. Metallic lead is bluish-gray; its surface recently cut exhibits a metallic lustre; it is soft, malleable, readily fusible. It evaporates at a white heat. Fused upon charcoal before the blowpipe it forms a coating of yellow oxide on the support. Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat; but dilute nitric acid dissolves it readily, more particularly on heating.

2. Oxide of lead is a yellow or reddish-yellow powder, looking brownish-red whilst hot, and fusible at a red heat. Hydrated oxide of lead is white. Both the oxide and its hydrate dissolve readily in nitric and acetic acids. Suboxide of lead ($Pb_2O$) is black, minium ($2\,PbO, PbO_2$) is red, the so-called sesquioxide is light brown, the binoxide is brown. They are all of them converted into the oxide by ignition in the air. The binoxide is not dissolved by heating with nitric acid, but it dissolves readily in that menstruum on addition of some spirit of wine. The solution contains nitrate of oxide of lead.

3. The salts of oxide of lead are non-volatile; most of them are colorless; the neutral soluble salts redden litmus-paper, and are decomposed at a red heat. If chloride of lead is ignited in the air, part of it volatilizes, and leaves behind a mixture of oxide of lead and chloride of lead.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce black precipitates of sulphide of lead (Pb S), which are insoluble in *cold* dilute acids, in alkalies, alkaline sulphides, and cyanide of potassium. Sulphide of lead is decomposed by hot nitric acid. If the acid was dilute, the whole of the lead is obtained in solution as nitrate of oxide of lead, and sulphur separates—if the acid was fuming, the sulphur is also completely oxidized, and insoluble sulphate of lead alone is obtained;—if the acid was of medium concentration, both processes take place, a portion of the lead being obtained in solution as nitrate of lead, whilst the remainder separates as sulphate of lead, together with the unoxidized sulphur. In solutions of salts of lead containing a large excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water or after partial neutralization of the free acid by an alkali. If a solution of lead is precipitated by hydrosulphuric acid in presence of a large quantity of free hydrochloric acid, a red precipitate is occasionally formed, consisting of chloride and sulphide of lead, which is however converted by an excess of hydrosulphuric acid into black sulphide of lead.

5. *Potassa, soda,* and *ammonia* throw down basic salts in the form of white precipitates, which are insoluble in ammonia but soluble in potassa and soda. In solutions of acetate of lead ammonia (free from carbonic acid) does not immediately produce a precipitate, owing to the formation of a soluble di- or triacetate of lead.

6. *Carbonate of soda* throws down a white precipitate of basic carbonate of lead [*e.g.*, $6\,[PbO, CO_2) + PbO, HO$], which is not quite

insoluble in a large excess of the precipitant, especially on heating, but is insoluble in cyanide of potassium.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions heavy white precipitates of CHLORIDE OF LEAD (Pb Cl), which are soluble in a large amount of water, especially upon application of heat. This chloride of lead is converted by ammonia into basic chloride of lead (Pb Cl, 3 Pb O + H O), which is also a white powder, but almost absolutely insoluble in water. In dilute nitric and hydrochloric acids chloride of lead is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce white precipitates of SULPHATE OF LEAD (Pb O, $S O_3$), which are nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the sulphate of lead precipitates only after some time, frequently only after a long time. It is advisable to add a considerable excess of dilute sulphuric acid, as this tends to increase the delicacy of the reaction, sulphate of lead being more insoluble in dilute sulphuric acid than in water. The separation of small quantities of sulphate of lead is best effected by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water; or, if allowable, with spirit. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa. It dissolves also pretty readily in the solutions of some of the salts of ammonia, particularly in solution of acetate of ammonia; dilute sulphuric acid precipitates it again from these solutions.

9. *Chromate of potassa* produces a yellow precipitate of CHROMATE OF LEAD (Pb O, $Cr O_3$), which is readily soluble in potassa, but difficultly so in dilute nitric acid.

10. If a mixture of a compound of lead with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, soft malleable METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a yellow incrustation of OXIDE OF LEAD. The reduction may be also readily effected by means of the stick of charcoal.

11. The *metallic incrustation* obtained according to p. 25, is black with brown edge, the *incrustation of oxide* is light yellow ochre, the *incrustation of iodide* varies from the yellow of the lemon to that of the yolk of an egg, the *incrustation of sulphide* varies from brownish-red to black, and is not dissolved by sulphide of ammonium (BUNSEN).

## § 118.

*Recapitulation and remarks.*—The metallic oxides of the first division of the fifth group are most distinctly characterized in their corresponding chlorides; since the different reactions of these chlorides with water and ammonia afford us a simple means both of detecting them and of effecting their separation from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the chloride of lead dissolves, whilst the chloride of silver and the subchloride of mercury remain undissolved. If these two chlorides are then treated with ammonia, the subchloride of mercury is converted into the black basic salt, insoluble in an excess of the ammonia, de-

scribed in § 116, 5, whilst the chloride of silver dissolves readily in the ammonia, and precipitates from this solution again upon addition of nitric acid. (When operating upon small quantities it is advisable first to expel the greater part of the ammonia by heat.) In the aqueous solution of chloride of lead the metal may be readily detected by sulphuric acid.

## SECOND DIVISION: OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

### § 119.

### *a.* Oxide of Mercury ($HgO$).

1. Oxide of mercury is generally crystalline, and has a bright red color, which upon reduction to powder changes to a dull yellowish-red; the oxide precipitated from solutions of the nitrate or chloride forms a yellow powder. It is not quite insoluble in water, it turns gray in the air. Upon exposure to heat it transiently acquires a deeper tint; at a dull red heat it is resolved into metallic mercury and oxygen. Both the crystalline and non-crystalline oxide dissolve readily in hydrochloric acid and in nitric acid.

2. The salts of oxide of mercury volatilize upon ignition; they suffer decomposition in this process; chloride, bromide, and iodide of mercury volatilize unaltered. On boiling a solution of the chloride, some of the salt escapes with the steam. Most of the salts are colorless. The soluble neutral salts redden litmus-paper. The nitrate and sulphate are decomposed by a large quantity of water into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrosulphuric acid* or *sulphide of ammonium* produces, after shaking, a perfectly white precipitate. Addition of a somewhat larger quantity of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color; an excess of the precipitant produces a black precipitate of sulphide of mercury ($HgS$). This progressive variation of color from white to black, which depends on the proportion of the hydrosulphuric acid or sulphide of ammonium added, distinguishes the oxide of mercury from all other bodies. The white precipitate which forms at first consists of a double compound of sulphide of mercury with the still undecomposed portion of the salt of oxide of mercury (in a solution of chloride of mercury, for instance, $HgCl + 2\,HgS$); the gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of color above mentioned. Sulphide of ammonium only dissolves the smallest traces of sulphide of mercury; the least amount of mercury is dissolved when the precipitate is digested in the heat with yellow sulphide of ammonium. Potassa and cyanide of potassium do not dissolve the sulphide of mercury, and it is entirely insoluble in hydrochloric and in nitric acid, even on boiling. By the very protracted action of hot concentrated nitric acid the precipitate is converted into a white body, consisting of $2\,HgS + HgO, NO_5$. Sulphide of potassium and sulphide of sodium in the presence of potash or soda dissolve the precipitate completely, but it is insoluble in double sulphide of potassium and hydrogen, and in double sulphide of sodium and hydrogen. Aqua

regia decomposes the precipitate and dissolves it with ease. In solutions of oxide of mercury containing a large excess of concentrated mineral acid, hydrosulphuric acid produces a precipitate only after addition of water.

4. *Potassa* added in small quantity produces in neutral or slightly acid solutions a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The reddish-brown precipitate is a BASIC SALT; the yellow precipitate consists of OXIDE OF MERCURY. An excess of the precipitant does not redissolve these precipitates. In very acid solutions this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of salts of ammonia potassa produces white precipitates. The precipitate thrown down by potassa from a solution of chloride of mercury containing an excess of chloride of ammonium is of analogous composition to the precipitate produced by ammonia (see 5).

5. *Ammonia* produces white precipitates quite analogous to those produced by potassa in presence of chloride of ammonium; thus, for instance, ammonia precipitates from solutions of chloride of mercury a CHLORIDE OF DIMERCUR-AMMONIUM ($N H_2Hg_2Cl$).

6. *Protochloride of tin* added in small quantity to solution of chloride of mercury, or to solutions of salts of oxide of mercury in presence of hydrochloric acid, throws down SUBCHLORIDE OF MERCURY ($2 HgCl + SnCl = Hg_2Cl + SnCl_2$). By addition of a larger quantity of the reagent the precipitated subchloride is reduced to METAL ($Hg_2Cl + SnCl = Hg_2 + SnCl_2$). The precipitate, which was white at first, acquires therefore now a gray tint, and may, after it has subsided, be readily united into globules of metallic mercury by boiling with hydrochloric acid and a little protochloride of tin.

7. If a little *galvanic element*, made out of a slip of platinum foil and a slip of tinfoil, joined at one end with a wooden clamp and otherwise apart from each other, is introduced into a solution of oxide of mercury acidified with hydrochloric acid, all the mercury will gradually be precipitated by preference upon the platinum. On removing the foils, drying and heating strongly in a glass tube, globules of mercury will be obtained, which may be more distinctly seen under the microscope. On heating this mercury with a fragment of iodine, it will be converted into red iodide of mercury (VAN DEN BROEK).

8. The salts of oxide of mercury show the same reaction as the salts of the suboxide with metallic *copper* and when heated with *carbonate of soda* in a glass tube.

## § 120.

### *b.* OXIDE OF COPPER (Cu O).

1. METALLIC COPPER has a peculiar red color, and a strong lustre; it is moderately hard, malleable, rather difficultly fusible; in contact with water and air it becomes covered with a green crust of basic carbonate of oxide of copper; upon ignition in the air it becomes coated over with suboxide and oxide. In hydrochloric acid and dilute sulphuric acid it is insoluble or nearly so, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into sulphate of oxide of copper, with evolution of sulphurous acid.

2. SUBOXIDE OF COPPER is red, its hydrate yellow; both change to

oxide upon ignition in the air. On treating the suboxide with dilute sulphuric acid metallic copper separates, whilst sulphate of oxide of copper dissolves; on treating suboxide of copper with hydrochloric acid white subchloride of copper is formed, which dissolves in an excess of the acid, but is reprecipitated from this solution by water.

3. OXIDE OF COPPER is a black fixed powder; its hydrate (Cu O, H O) is of a light blue color. Both the oxide of copper and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids.

4. Most of the neutral SALTS OF OXIDE OF COPPER are soluble in water; the soluble salts redden litmus, and suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; the hydrated salts are usually of a blue or green color, which their solutions continue to exhibit even when much diluted.

5. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions brownish-black precipitates of SULPHIDE OF COPPER (Cu S). This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of sulphide of potassium and sulphide of sodium fail also to dissolve it or dissolve it only to a very trifling extent; but it is a little more soluble in sulphide of ammonium, especially when yellow and hot. The latter reagent is therefore not well adapted to effect the perfect separation of sulphide of copper from other metallic sulphides. Sulphide of copper is readily decomposed and dissolved by boiling nitric acid, but it remains altogether unaffected by boiling dilute sulphuric acid. It dissolves completely in solution of cyanide of potassium. In solutions of salts of copper which contain a very large excess of a concentrated mineral acid hydrosulphuric acid produces a precipitate only after the addition of water.

6. *Potassa* or *soda* produces a light blue bulky precipitate of HYDRATE OF OXIDE OF COPPER (Cu O, H O). If the solution is highly concentrated, and the precipitant is added in excess, the precipitate turns black after the lapse of some time, and loses its bulkiness, even in the cold; but the change takes place immediately if the precipitate is boiled with the fluid in which it is suspended (and which must, if necessary, be diluted for the purpose). In this process the Cu O, H O is converted into 3 Cu O, H O.

7. *Carbonate of soda* produces a greenish-blue precipitate of HYDRATED BASIC CARBONATE OF COPPER ($Cu\,O, C\,O_2 + Cu\,O, H\,O$), which upon boiling changes to brownish-black hydrate of oxide of copper, and dissolves in ammonia to an azure-blue, and in cyanide of potassium to a colorless fluid.

8. *Ammonia* added in small quantity to solutions of neutral salts produces a greenish-blue precipitate, consisting of a BASIC SALT OF COPPER. This precipitate redissolves readily upon further addition of ammonia to a perfectly clear fluid of a magnificent azure-blue, which owes its color to the formation of a BASIC SALT OF AMMONIA AND OXIDE OF COPPER. Thus, for instance, in a solution of sulphate of oxide of copper ammonia produces a precipitate of $N\,H_3$, $Cu\,O + N\,H_4O$, $S\,O_3$. In solutions containing a certain amount of free acid ammonia produces no precipitate, but this azure-blue coloration makes its appearance at once the instant the ammonia predominates. The blue color ceases to be perceptible only in very dilute solutions. Potassa produces in such blue solutions in the cold, after the lapse of some time, a preci-

pitate of blue hydrate of oxide of copper; but upon boiling the fluid this reagent precipitates the whole of the copper as black hydrated oxide. Carbonate of ammonia shows the same reactions as ammonia.

N.B. In the presence of non-volatile organic acids the salts of copper are not precipitated by caustic or carbonated alkalies, the resulting solutions having a deep blue color. In presence of sugar or similar organic substances caustic alkalies produce precipitates which are soluble in excess of the precipitants; carbonate of soda, however, produces a permanent precipitate.

9. *Ferrocyanide of potassium* produces in moderately dilute solutions a reddish-brown precipitate of FERROCYANIDE OF COPPER ($Cu_2$, Cfy), insoluble in dilute acids, but decomposed by potassa. In very highly dilute solutions the reagent merely produces a reddish coloration.

10. If the solution of a salt of oxide of copper is mixed with sulphurous acid or with hydrochloric acid and sulphite of soda, and *sulphocyanide of potassium* is then added, the SUBSULPHOCYANIDE OF COPPER ($Cu_2$, Cy $S_2$) is thrown down. The precipitate is white, and is practically insoluble in water and dilute acids.

11. *Metallic iron* when brought into contact with concentrated solutions of salts of copper is almost immediately covered with a copper-red coating of METALLIC COPPER; very dilute solutions produce this coating only after some time. Presence of a little free acid accelerates the reaction. If a fluid containing copper and a little free hydrochloric acid is poured into a *platinum capsule* (the lid of a platinum crucible), and a small piece of *zinc* is introduced, the bright platinum surface speedily becomes covered with a COATING OF COPPER; even with very dilute solutions this coating is clearly discernible. If a piece of iron wire is inserted into a spiral formed from a rather stout *platinum wire*, and the whole is then placed in a slightly acidified solution of copper, the platinum wire will after some time be found to be coated with COPPER.

12. If a mixture of a compound of copper with *carbonate of soda* is exposed on a charcoal support to the *inner flame of the blowpipe*, METALLIC COPPER is obtained, without incrustation of the charcoal. The reduction may be also very conveniently effected in the stick of charcoal (p. 24). The best method of freeing the copper from the particles of charcoal is to triturate the fused mass in a small mortar with water, and to wash off the charcoal powder, when the copper-red metallic particles will be left behind.

13. If copper, or some alloy containing copper, or a trace of a salt of copper, or even simply the loop of a platinum wire dipped in a highly dilute copper solution, is introduced into the fusing zone of the *gas flame*, or exposed to the inner *blowpipe flame*, the upper or outer portion of the flame shows a magnificent emerald-green tint. Addition of hydrochloric acid to the sample considerably heightens the beauty and delicacy of this reaction. The flame then has an azure color.

14. *Borax* readily dissolves oxide of copper in the outer gas- or blowpipe-flame. The beads are green while hot, blue when cold. In the inner flame the bead is colorless unless a very large quantity of copper is present; when cold it is red and opaque. In the lower reducing zone of the Bunsen gas flame the bead does not become reddish-brown until the addition of binoxide of tin, when this change rapidly takes place, owing to the production of suboxide of copper. If the bead

is introduced alternately into the lower oxidizing zone and the lower reducing zone, it becomes ruby red and transparent.

## § 121.

### *c.* TEROXIDE OF BISMUTH ($BiO_3$).

1. BISMUTH has a reddish tin-white color and moderate metallic lustre; it is of medium hardness, brittle, readily fusible; fused upon a charcoal support it forms an incrustation of yellow teroxide. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into sulphate of teroxide of bismuth, with evolution of sulphurous acid.

2. The TEROXIDE OF BISMUTH is a yellow powder, which transiently acquires a deeper tint when heated. It fuses at a red heat. Hydrate of teroxide of bismuth is white. Both the teroxide and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids. The grayish-black BINOXIDE OF BISMUTH and the red BISMUTHIC ACID ($BiO_2$) are converted into teroxide by ignition in the air. By heating with nitric acid they are converted into nitrate of teroxide of bismuth.

3. The SALTS OF TEROXIDE OF BISMUTH are non-volatile; most of them are decomposed at a red heat. Terchloride of bismuth is volatile. The salts of teroxide of bismuth are colorless or white; some of them are soluble in water, others insoluble. The soluble salts in the neutral state redden litmus paper; they are decomposed by a large quantity of water into insoluble basic salts, which separate, whilst the greater portion of the acid remains in solution together with some teroxide of bismuth.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in neutral and acid solutions black precipitates of TERSULPHIDE OF BISMUTH, which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium, but are readily decomposed and dissolved by boiling nitric acid. In solutions of salts of bismuth which contain a very considerable excess of hydrochloric or nitric acid, hydrosulphuric acid produces a precipitate only after the addition of water.

5. *Potassa* and *ammonia* throw down HYDRATE OF TEROXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitant.

6. *Carbonate of soda* and *carbonate of ammonia* throw down BASIC CARBONATE OF TEROXIDE OF BISMUTH ($BiO_3, CO_2$), as a white bulky precipitate, which is insoluble in excess of the precipitant, and in cyanide of potassium. Warming assists the precipitation.

7. *Bichromate of potassa* precipitates CHROMATE OF TEROXIDE OF BISMUTH ($BiO_3, 2CrO_3$) as a yellow powder. This substance differs from chromate of lead in being readily soluble in dilute nitric acid and insoluble in potassa.

8. *Dilute sulphuric acid* fails to precipitate moderately dilute solutions of nitrate of teroxide of bismuth. On evaporating with an excess of sulphuric acid on the water-bath to dryness, a white saline mass is left, which always dissolves readily to a clear fluid in water acidified with sulphuric acid (characteristic difference between teroxide of bismuth

and oxide of lead). After long standing (several days occasionally) basic sulphate of teroxide of bismuth ($BiO_3, SO_3, + 2$ aq.) separates from this solution in white microscopic needle-shaped crystals, which dissolve in nitric acid.

9. The reaction which characterizes the teroxide of bismuth more particularly is the decomposition of its neutral salts by *water*, which is attended with separation of insoluble basic salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. This reaction is the most sensitive with terchloride of bismuth, as the BASIC CHLORIDE OF BISMUTH ($BiCl_3, 2BiO_3$) is almost absolutely insoluble in water. Where water fails to precipitate nitric acid solutions of bismuth, owing to the presence of too much free acid, a precipitate will almost invariably make its appearance immediately upon addition of solution of chloride of sodium or chloride of ammonium. Presence of tartaric acid does not interfere with the precipitation of bismuth by water.

10. On mixing a solution of bismuth with an excess of solution of protochloride of tin in potassa or soda, a black precipitate of binoxide of bismuth will fall. This is a very characteristic and delicate reaction.

11. If a mixture of a compound of bismuth with *carbonate of soda* is exposed on a charcoal support to the *reducing flame*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight incrustation of TEROXIDE OF BISMUTH, which is orange-colored whilst hot, yellow when cold. The reduction may be also conveniently effected in the stick of charcoal (p. 24). On triturating the end of the charcoal stick containing the reduced metal, yellowish spangles will be obtained.

12. The *metallic incrustation*, obtained according to p. 25, is black with a brown edge. The *incrustation of oxide* is yellowish white; it is turned black by protochloride of tin and soda, see 10 (difference from the incrustation of oxide of lead). The *incrustation of iodide* is bluish brown with red edge. The *incrustation of sulphide* is umber-colored with coffee colored edge, not dissolved by sulphide of ammonium (BUNSEN).

## § 122.

### *d.* OXIDE OF CADMIUM (CdO).

1. METALLIC CADMIUM has a tin-white color; it is lustrous, not very hard, malleable; it fuses at a temperature below red heat, and volatilizes at a temperature somewhat above the boiling point of mercury, and may accordingly easily be sublimed in a glass tube. Heated on charcoal before the blowpipe it takes fire and burns, emitting brown fumes of oxide of cadmium, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen; but nitric acid dissolves it most readily.

2. OXIDE OF CADMIUM is a brown, fixed powder; its hydrate is white. Both the oxide and its hydrate dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The SALTS OF OXIDE OF CADMIUM are colorless or white; some of them are soluble in water. The soluble salts in the neutral state redden litmus-paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions, bright yellow precipitates of SULPHIDE OF CADMIUM (Cd S), which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium (difference from copper). They are readily decomposed and dissolved by boiling nitric acid, as well as by boiling hydrochloric acid and by boiling dilute sulphuric acid (difference from copper). In solutions of salts of cadmium containing a large excess of acid, hydrosulphuric acid produces a precipitate only after dilution with water.

5. *Potassa* and *soda* produce white precipitates of HYDRATE OF OXIDE OF CADMIUM (Cd O, H O), which are insoluble in an excess of the precipitants.

6. *Ammonia* likewise precipitates white HYDRATE OF OXIDE OF CADMIUM, which however redissolves readily and completely to a colorless fluid in an excess of the precipitant.

7. *Carbonate of soda* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM (Cd O, $C O_2$), which are insoluble in an excess of the precipitants. The presence of salts of ammonia impedes the precipitation; free ammonia prevents it. The precipitate is readily soluble in cyanide of potassium. It takes some time to separate from dilute solutions; warming assists the separation greatly.

8. *Sulphocyanide of potassium* does not throw down solutions of cadmium, even after the addition of sulphurous acid (difference from copper).

9. If a mixture of a compound of cadmium with *carbonate of soda* is exposed on a charcoal support to the *reducing flame*, the charcoal becomes covered with a brownish yellow coating of OXIDE OF CADMIUM, owing to the instant volatilization of the reduced metal and its subsequent re-oxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

10. The *metallic incrustation* obtained according to p. 25 is black with brown edge. The *incrustation of oxide* is brownish black, the edge passing from brown to white. The *incrustation of iodide* is white. The *incrustation of sulphide* is lemon yellow, not dissolved by sulphide of ammonium (BUNSEN.)

## § 123.

*Recapitulation and remarks.*—The perfect separation of the metallic oxides of the second division of the fifth group from suboxide of mercury and oxide of silver may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. Traces of salt of oxide of mercury, which are at first retained by the precipitated chloride of silver by surface attraction, are dissolved out completely by washing (G. J. MULDER). The oxide of mercury is distinguished from the other oxides of this division by the insolubility of the corresponding sulphide in boiling nitric acid. This property affords a convenient means for its separation. Only care must always be taken to free the sulphides completely by washing from all traces of hydrochloric acid or a chloride that may happen to be present, before proceeding to boil them with nitric acid. Moreover, the reactions with protochloride of tin or with metallic copper, as well as those in the dry way, will, after the previous removal of the suboxide, always readily indicate the presence of oxide of mercury. When the moist

way is chosen, the sulphide of mercury is dissolved most conveniently by heating it with hydrochloric acid and a small crystal of chlorate of potassa.

From the still remaining oxides the oxide of lead is separated by addition of sulphuric acid. The separation is the most complete if the fluid, after addition of dilute sulphuric acid in excess, is evaporated on the water-bath, the residue diluted with water, slightly acidified with sulphuric acid, and the undissolved sulphate of lead filtered off immediately. The sulphate of lead may be further examined in the dry way by the reaction described in § 117, 10, or also as follows:—Pour over a small portion of the sulphate of lead a little of a solution of chromate of potassa, and apply heat, which will convert the white precipitate into yellow chromate of lead. Wash this, add a little solution of potassa or soda, and heat; the precipitate will now dissolve to a clear fluid; by acidifying this fluid with acetic acid, a yellow precipitate of chromate of lead will again be produced. After the removal of the oxides of mercury and lead, the teroxide of bismuth may be separated from oxide of copper and oxide of cadmium by addition of ammonia in excess, as the latter two oxides are soluble in an excess of this agent. If the precipitate, after being filtered off, is dissolved in one or two drops of hydrochloric acid on a watchglass, and water added, the appearance of a milky turbidity is a confirmation of the presence of bismuth.—The presence of a notable quantity of oxide of copper is revealed by the blue color of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then ferrocyanide of potassium. The separation of oxide of copper from oxide of cadmium may be effected by evaporating the ammoniacal solution to a small bulk, acidifying with hydrochloric acid, adding a little sulphurous acid and sulphocyanide of potassium, filtering off the subsulphocyanide of copper, and precipitating the cadmium in the filtrate by hydrosulphuric acid (an unnecessarily large excess of sulphurous acid must of course be avoided.) The separation of oxide of copper from oxide of cadmium may also be effected by acting on the sulphides with cyanide of potassium or with boiling dilute sulphuric acid (5 parts of water to 1 part of concentrated acid.) In the two latter methods the solution of the copper and cadmium is precipitated by hydrosulphuric acid, and the precipitate separated from the fluid by decantation or filtration. On treating the precipitate now with some water and a small lump of cyanide of potassium, the sulphide of copper will dissolve, leaving the yellow sulphide of cadmium undissolved. By boiling the precipitate of the mixed sulphides, on the other hand, with dilute sulphuric acid, the sulphide of copper remains undissolved, whilst the sulphide of cadmium is obtained in solution. Hydrosulphuric acid will therefore now throw down from the filtrate yellow sulphide of cadmium (A. W. Hofmann).

### *Special Reactions of the rarer Oxides of the fifth group.*

### § 124.

#### a. Protoxide of Palladium (Pd O).

Palladium is found in the metallic state, occasionally alloyed with gold and silver, but more particularly in platinum ores. It greatly resembles platinum, but is somewhat darker in color. It fuses with great difficulty. Heated in the air to dull redness

it becomes covered with a blue film: but it recovers its light color and metallic lustre upon more intense ignition. It is sparingly soluble in pure nitric acid, but dissolves somewhat more readily in nitric acid containing nitrous acid; it dissolves very sparingly in boiling concentrated sulphuric acid, but it is soluble in fusing bisulphate of potassa, and readily soluble in nitrohydrochloric acid. There are three oxides, the suboxide ($Pd_2O$), the protoxide, and the binoxide. PROTOXIDE OF PALLADIUM is black, its hydrate dark-brown; both are by intense ignition resolved into oxygen and metallic palladium. BINOXIDE OF PALLADIUM is black; by heating with dilute hydrochloric acid it is dissolved to protochloride, with evolution of chlorine. The SALTS OF PROTOXIDE OF PALLADIUM are mostly soluble in water; they are brown or reddish-brown; their concentrated solutions are reddish-brown, their dilute solutions yellow. Water precipitates from a solution of nitrate of protoxide of palladium containing a slight excess of acid a brown basic salt. The oxygen salts, as well as the protochloride, are decomposed by ignition, leaving metallic palladium behind. *Hydrosulphuric acid* and *sulphide of ammonium* throw down from acid or neutral solutions black protosulphide of palladium, which does not dissolve in sulphide of ammonium, but is soluble in boiling hydrochloric acid, and readily soluble in nitrohydrochloric acid. From the solution of the protochloride *potassa* precipitates a brown basic salt, soluble in an excess of the precipitant; *ammonia* flesh-colored ammonio-protochloride of palladium ($Pd Cl, N H_3$) soluble in excess of ammonia to a colorless fluid, from which hydrochloric acid throws down yellow crystalline chloride of palladium-ammonium ($N Pd H_3, Cl$). *Cyanide of mercury* throws down yellowish-white protocyanide of palladium as a gelatinous precipitate, slightly soluble in hydrochloric acid, readily soluble in ammonia (especially characteristic). *Protochloride of tin* produces, in absence of free hydrochloric acid, a brownish-black precipitate; in presence of free hydrochloric acid, a red-colored solution, which speedily turns brown and ultimately green, and upon addition of water brownish-red. *Sulphate of protoxide of iron* produces a deposit of palladium on the sides of the glass. *Iodide of potassium* precipitates black protiodide of palladium (very characteristic). *Chloride of potassium* precipitates from highly concentrated solutions potassio-protochloride of palladium (K Cl, Pd Cl), in the form of golden-yellow needles, which dissolve readily in water to a dark-red fluid, but are insoluble in absolute alcohol. *Nitrite of potassa* produces in not too dilute solutions a yellowish, crystalline precipitate which becomes reddish on long standing and is soluble in much water. *Sulphocyanide of potassium* does not precipitate palladium, even after the addition of sulphurous acid (difference from copper, and best means of separating from the same). On treatment with *carbonate of soda* in the upper oxidizing flame (p. 23) all the compounds of palladium yield a gray metallic sponge.

### *b.* SESQUIOXIDE OF RHODIUM ($Ro_2O_3$).

RHODIUM is found in small quantity in platinum ores. It is almost silver white, very malleable, and difficultly fusible. When prepared in the wet way it is a gray powder. The powder when ignited in the air absorbs oxygen, which it gives up again upon stronger ignition. Rhodium is insoluble in all acids; it dissolves in aqua regia only when alloyed with platinum, copper, &c., and not when alloyed with gold or silver. Fusing metaphosphoric acid and fusing bisulphate of potassa dissolve it, forming a salt of the sesquioxide. There are four oxides: the protoxide, sesquioxide (base of the salts), binoxide, and tetroxide (a weak acid). The SESQUIOXIDE is gray, it forms a yellow and a brownish-black hydrate; it is insoluble in acids, but dissolves in fusing metaphosphoric acid and in fusing bisulphate of potassa. The solutions are rose-colored. *Sulphuretted hydrogen* and *sulphide of ammonium* precipitate in time, especially when assisted by heat, a brown sulphide, which is insoluble in sulphide of ammonium, but dissolves in boiling nitric acid. *Potassa*, if added in not too large excess, throws down at once yellow $Ro_2O_3, 5 H O$, which is soluble in excess of the precipitant at the ordinary temperature; on boiling the solution, blackish-brown $Ro_2O_3, 3 H O$ is precipitated. In a solution of the sesquichloride, potassa at first produces no precipitate, but, on addition of alcohol, black $Ro_2O_3, 3 H O$ separates soon (CLAUS). *Ammonia* produces after some time a yellow precipitate, soluble in hydrochloric acid. *Zinc* precipitates black metallic rhodium. On heating with *nitrite of potassa*, the sesquichloride of rhodium becomes yellow, and an orange-yellow precipitate is formed, which is slightly soluble in water, but readily soluble in hydrochloric acid; at the same time another portion of the rhodium is converted into a yellow salt, which remains in solution and is precipitated by alcohol (GIBBS). All solid compounds of rhodium, on ignition in *hydrogen*, or on ignition on a platinum wire with carbonate of soda in the upper oxidizing flame, yield the metal, which is well charac-

terized by its insolubility in aqua regia, its solubility in fusing bisulphate of potassa, and the behaviour of its solution to potassa and alcohol.

### c. Oxides of Osmium.

Osmium is found in platinum ores as a native alloy of osmium and iridium. It is generally obtained as a black powder, or gray and with metallic lustre; it is infusible. The metal, the protoxide (Os O), and the binoxide oxidize readily when heated to redness in the air, and give osmic acid ($Os O_4$), which volatilizes and makes its presence speedily known by its peculiar exceedingly irritating and offensive smell, resembling that of chlorine and iodine (highly characteristic). If a little osmium on a strip of platinum foil is held in the outer mantle of a *gas or alcohol flame*, at half height, the flame becomes most strikingly luminous. Even minute traces of osmium may by this reaction be detected in alloys of iridium and osmium; but the reaction is in that case only momentary; it may however be reproduced by holding the sample first in the reducing flame, then again in the outer mantle. *Nitric acid*, more particularly red fuming nitric acid, and aqua regia dissolve osmium to osmic acid. Application of heat promotes the solution, which is however attended in that case with volatilization of osmic acid. Very intensely ignited osmium is insoluble in acids. It is fused with nitrate of potassa, and the fused mass distilled with nitric acid; the osmic acid is found in the distillate. By heating osmium in dry *chlorine* free from air, first bluish-black protochloride is formed, but always only in small quantity, then the more volatile and red bichloride; if moist chlorine is used, a green mixture of both chlorides is formed. The protochloride dissolves with a blue color, the bichloride with a yellow color, and both together with a green color, which turns red. The solutions are soon decomposed, osmic acid, hydrochloric acid, and a mixture of protoxide and binoxide, being formed, the mixed oxides separating as a black powder. On heating a mixture of powder of osmium, or of sulphide of osmium, and chloride of potassium, in chlorine, a double salt of bichloride of osmium and chloride of potassium is produced in the form of octahedra, which are slightly soluble in water and insoluble in alcohol. The solution of this double salt is more permanent than that of the bichloride. Potassa decolorizes the solution; on boiling bluish-black, hydrated binoxide of osmium separates. On fusing the double chloride with carbonate of soda, dark gray binoxide of osmium separates. The anhydrous osmic acid has no effect on litmus, and cannot form salts. It is white, crystalline, fusible at a gentle heat, and boils at about 100°; the fumes attack the nose and eyes powerfully. Heated with water, it fuses and dissolves, but slowly. The solution has an irritating, unpleasant smell. *Alkalies* color the solution yellow in consequence of the formation of osmite of potassa ($K O, Os O_2$); on distilling, the greater part of the osmic acid passes over (very characteristic), the remainder splits into oxygen and osmious acid, or on boiling into osmic acid, binoxide of osmium, and potassa. Osmic acid decolorizes *indigo solution*, separates iodine from *iodide of potassium*, converts *alcohol* into aldehyde and acetic acid. *Nitrite of potassa* readily reduces it to osmite of potassa. *Hydrosulphuric acid* precipitates brownish-black sulphide, which only separates when a strong acid is present; the precipitate is insoluble in sulphide of ammonium. *Sulphite of soda* produces a deep violet coloration, and dark-blue sulphite of protoxide of osmium gradually separates, especially on evaporating or warming with sulphate or carbonate of soda. *Sulphate of iron* produces a black precipitate of binoxide. *Protochloride of tin* produces a brown precipitate, soluble in hydrochloric acid to a brown fluid. *Zinc* and many metals in the presence of a strong acid precipitate metallic osmium. All the compounds of osmium yield the metal on ignition in a current of *hydrogen*.

### d. Oxides of Ruthenium.

Ruthenium is found in small quantity in platinum ores. It is a grayish-white brittle and very difficultly fusible metal. It is barely acted upon by aqua regia; fusing bisulphate of potassa fails altogether to affect it. By ignition in the air it is converted into bluish-black sesquioxide insoluble in acids; by ignition with chloride of potassium in a current of chlorine gas into potassio-sesquichloride of ruthenium; by fusion with nitrate of potassa, with hydrate of potassa, or with chlorate of potassa, into ruthenate of potassa ($K O, Ru O_3$). The fused mass obtained in the latter case is greenish-black, and dissolves to an orange-colored fluid, which tinges the skin black, from separation of black oxide. Acids throw down from the solution black sesquioxide, which dissolves in hydrochloric acid to an orange-yellow fluid. This solution is resolved by heat into hydrochloric acid and brownish-black sesquioxide. In a concentrated state it gives with chloride of potassium and chloride of ammonium crystalline glossy-

violet precipitates, which on boiling with water deposit black oxyprotochloride. *Potassa* precipitates black hydrate of sesquioxide of ruthenium, which is insoluble in alkalies, but dissolves in acids. *Hydrosulphuric acid gas* causes at first no alteration; but after some time the fluid acquires an azure-blue tint, and deposits brown sulphide of ruthenium (very characteristic). *Sulphide of ammonium* produces brownish-black precipitates, barely soluble in an excess of the precipitant. *Sulphocyanide of potassium* produces—in the absence of other metals of the platinum ores—after some time a red coloration, which gradually changes to purple-red, and upon heating to a fine violet tint (very characteristic). *Zinc* produces at first an azure-blue coloration, which subsequently disappears, ruthenium being deposited at the same time in the metallic state. *Nitrite of potassa* colors the solution yellow, with the formation of a double salt, which is readily soluble in water and alcohol. The alkaline solution of this double salt, when mixed with a little colorless sulphide of ammonium, turns crimson (characteristic); on the addition of more sulphide of ammonium, sulphide of ruthenium is precipitated.

## § 125.

### SIXTH GROUP.

More common oxides:—TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE OF ANTIMONY, ARSENIOUS ACID AND ARSENIC ACID.

Rarer oxides:—Oxides of IRIDIUM, MOLYBDENUM, TUNGSTEN, TELLURIUM, SELENIUM.

The higher oxides of the elements belonging to the sixth group are all of them more or less strongly pronounced acids. But we class them here with the bases, as they cannot well be separated from the lower degrees of oxidation of the same elements, to which they are very closely allied in their reactions with hydrosulphuric acid.

*Properties of the group.*—The sulphides corresponding to the oxides of the sixth group are insoluble in dilute acids. These combine with alkaline sulphides (either immediately, or with the aid of sulphur) to soluble sulphur salts, in which they take the part of the acid. Hydrosulphuric acid precipitates these oxides therefore, like those of the fifth group, completely from acidified solutions. The precipitated sulphides differ however from those of the fifth group in this, that they dissolve in sulphide of ammonium, sulphide of potassium, &c., and are reprecipitated from these solutions by addition of acids.

We divide the more common oxides of this group into two classes, and distinguish,

1. OXIDES WHOSE CORRESPONDING SULPHIDES ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, and are reduced to the metallic state upon fusion with nitrate and carbonate of soda: viz., TEROXIDE OF GOLD and BINOXIDE OF PLATINUM.

2. OXIDES WHOSE CORRESPONDING SULPHIDES ARE SOLUBLE IN BOILING HYDROCHLORIC ACID OR NITRIC ACID, and are upon fusion with nitrate and carbonate of soda converted into oxides or acids: viz., TEROXIDE OF ANTIMONY, PROTOXIDE and BINOXIDE OF TIN, ARSENIOUS and ARSENIC ACIDS.

FIRST DIVISION.

*Special Reactions.*

## § 126.

### a. Teroxide of Gold ($Au_2O_3$).

1. Metallic gold has a reddish-yellow color and a high metallic lustre: it is rather soft, exceedingly malleable, difficultly fusible: it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids; but it dissolves in fluids containing or evolving chlorine, *e.g.*, in nitrohydrochloric acid. The solution contains terchloride of gold.

2. Teroxide of gold is a blackish-brown, its hydrate a chestnut brown powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little teroxide of gold; water reprecipitates it from these solutions. Protoxide of gold (AuO) is violet-black; it is decomposed by heat into gold and oxygen.

3. Oxygen salts of gold are practically unknown. The haloid salts are yellow, and their solutions continue to exhibit this color up to a high degree of dilution. The whole of them are readily decomposed by ignition. Neutral solution of terchloride of gold reddens litmus-paper.

4. *Hydrosulphuric acid* precipitates from neutral or acid solutions the whole of the metal, from cold solutions as tersulphide of gold, from boiling solutions as protosulphide of gold ($AuS$). The precipitates are insoluble in hydrochloric and in nitric acid, but soluble in nitrohydrochloric acid. They are insoluble in colorless sulphide of ammonium, but soluble in yellow sulphide of ammonium, and more readily still in yellow sulphide of sodium or sulphide of potassium.

5. *Sulphide of ammonium* precipitates brownish-black tersulphide of gold, which redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

6. *Ammonia* produces, though only in concentrated solutions of gold, reddish-yellow precipitates of *fulminating gold*. The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Protochloride of tin* containing an admixture of *bichloride* (which may be easily prepared by mixing solution of protochloride of tin with a little chlorine-water), produces even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of purple of Cassius, is insoluble in hydrochloric acid. It is assumed to be a hydrated compound of binoxide of tin and protoxide of gold with protoxide and binoxide of tin ($AuO, SnO_2 + SnO, SnO_2 + 4HO$).

8. *Salts of protoxide of iron* reduce the terchloride of gold in its solutions, and precipitate metallic gold in form of a most minutely divided brown powder. The fluid in which the precipitate is suspended

appears of a blackish-blue color by transmitted light. The dried precipitate shows metallic lustre when pressed with the blade of a knife.

9. *Nitrite of potassa* produces a precipitate of metallic gold. In very dilute solutions the fluid at first only appears colored blue, but in time the whole of the gold separates.

10. Potassa or soda added in excess to terchloride of gold leaves the fluid clear, but upon addition of *tannic acid* metallic gold separates. Warming assists the precipitation.

11. All compounds of gold are reduced in the *stick of charcoal* (p. 24). By triturating the charcoal afterwards, spangles of metal will be obtained, which are insoluble in nitric acid, but readily soluble in aqua regia.

## § 127.

### *b.* Binoxide of Platinum ($PtO_2$).

1. Metallic platinum has a light steel-gray color; it is very lustrous, moderately hard, very difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids. It dissolves in nitrohydrochloric acid, especially upon heating. The solution contains bichloride of platinum.

2. Binoxide of platinum is a blackish-brown, its hydrate a reddish-brown powder. Both are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids. The protoxide of platinum (PtO) is black, its hydrate brown; they are both by ignition reduced to the metallic state.

3. The salts of binoxide of platinum are decomposed at a red heat. They are yellow. Bichloride of platinum is reddish-brown, its solution reddish-yellow, which tint it retains up to a high degree of dilution. The solution reddens litmus-paper. Exposure to a very low red heat converts bichloride of platinum to protochloride (PtCl); application of a stronger red heat reduces it to the metallic state. Solution of bichloride of platinum containing protochloride has a deep brown color.

4. *Hydrosulphuric acid* throws down from acid and neutral solutions, but always only after the lapse of some time, a blackish-brown precipitate of bisulphide of platinum. If the solution is heated after the addition of the hydrosulphuric acid the precipitate forms immediately. It dissolves in a great excess of alkaline sulphides, more particularly of the higher degrees of sulphuration. Bisulphide of platinum is insoluble in hydrochloric acid and in nitric acid; but it dissolves in nitrohydrochloric acid.

5. *Sulphide of ammonium* produces the same precipitate; this redissolves completely, though slowly and with difficulty, in a large excess of the precipitant if the latter contains an excess of sulphur. Acids reprecipitate the bisulphide of platinum unaltered from the reddish-brown solution.

6. *Chloride of potassium* and *chloride of ammonium* (and accordingly of course also potassa and ammonia in presence of hydrochloric acid) produce in not too highly dilute solutions of bichloride of platinum yellow crystalline precipitates of potassio- and ammonio-bichloride of platinum, which are as insoluble in acids as in water, but are dissolved by heating with solution of potassa. From dilute solutions these precipi-

nates are obtained by evaporating the fluid mixed with the precipitants on the water-bath, and treating the residue with a little water or with dilute spirit of wine. Upon ignition ammonio-bichloride of platinum leaves spongy platinum behind; potassio-bichloride leaves platinum and chloride of potassium. The decomposition of the latter compound is complete only if the ignition is effected in a current of hydrogen gas or with addition of some oxalic acid.

7. *Protochloride of tin* imparts to solutions containing much free hydrochloric acid an intensely dark brownish-red color, owing to a reduction of the bichloride of platinum to protochloride. But the reagent produces no precipitate in such solutions.

8. *Sulphate of protoxide of iron* does not precipitate solution of bichloride of platinum, except upon very long-continued boiling, in which case the platinum ultimately suffers reduction.

9. On igniting a compound of platinum mixed with carbonate of soda on the loop of a platinum wire in the upper *oxidizing flame*, a gray spongy mass is obtained, which on trituration in an agate mortar yields silvery spangles, insoluble in hydrochloric and nitric acid, but soluble in aqua regia.

## § 128.

*Recapitulation and remarks.*—The reactions of gold and platinum enable us, at least partially, to detect those two metals in the presence of many other oxides, and more particularly where platinum and gold are present in the same solution. In the latter case the solution is most conveniently evaporated to dryness at a gentle heat with chloride of ammonium, and the residue treated with dilute spirit of wine, in order to obtain the gold in solution and the platinum in the residue. The precipitate will thus give platinum by ignition, and the gold may be precipitated from the solution by sulphate of protoxide of iron, after removing the spirit of wine by evaporation.

## SECOND DIVISION.

### *Special Reactions.*

## § 129.

### *a.* Protoxide of Tin ($SnO$).

1. Tin has a light grayish-white color and a high metallic lustre; it is soft and malleable; when bent it produces a crackling sound. Heated in the air it absorbs oxygen and is converted into grayish-white binoxide; heated on charcoal before the blowpipe it forms a white incrustation. Concentrated hydrochloric acid dissolves tin to protochloride, with evolution of hydrogen gas; nitrohydrochloric acid dissolves it, according to circumstances, to bichloride or to a mixture of proto- and bichloride. Tin dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into sulphate of binoxide; moderately concentrated nitric acid oxidizes it readily, particularly with the aid of heat; the white binoxide formed (hydrate of metastannic acid, $SnO_2, 2HO$) does not redissolve in an excess of the acid.

2. PROTOXIDE OF TIN is a black or grayish-black powder; its hydrate is white. Protoxide of tin is reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into hydrate of metastannic acid, which is insoluble in an excess of the acid.

3. The SALTS OF PROTOXIDE OF TIN are colorless; they are decomposed by heat. The soluble salts, in the neutral state, redden litmus-paper. The salts of protoxide of tin rapidly absorb oxygen from the air, and are partially or entirely converted into salts of binoxide. Protochloride of tin, no matter whether in crystals or in solution, also absorbs oxygen from the air, which leads to the formation of insoluble oxy-protochloride of tin and bichloride of tin. Hence a solution of protochloride of tin becomes speedily turbid if the bottle is often opened and there is only little free acid present; and hence it is only quite recently prepared protochloride of tin which will completely dissolve in water free from air, whilst crystals of protochloride of tin that have been kept for any time will dissolve to a clear fluid only in water containing hydrochloric acid.

4. *Hydrosulphuric acid* throws down from neutral and acid solutions a dark brown precipitate of hydrated PROTOSULPHIDE OF TIN (Sn S). This reagent does not precipitate alkaline solutions, or at least not completely. The precipitation may be prevented by the presence of a very large quantity of free hydrochloric acid. The precipitate is insoluble, or nearly so, in protosulphide of ammonium, but dissolves readily in the higher yellow sulphide. Acids precipitate from this solution yellow bisulphide of tin, mixed with sulphur. Protosulphide of tin dissolves also in solution of soda and potassa. Acids precipitate from these solutions brown protosulphide. Boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid; boiling nitric acid converts it into insoluble hydrate of metastannic acid.

5. *Sulphide of ammonium* produces the same precipitate of hydrated PROTOSULPHIDE OF TIN.

6. *Potassa, soda, ammonia,* and *carbonates of the alkalies* produce a white bulky precipitate of HYDRATE OF PROTOXIDE OF TIN (Sn O, H O), which redissolves readily in an excess of potassa or soda, but is insoluble in an excess of the other precipitants. If the solution of hydrate of protoxide of tin in potassa is briskly evaporated a compound of binoxide of tin and potassa is formed, which remains in solution, whilst metallic tin precipitates; but upon evaporating slowly crystalline anhydrous protoxide of tin separates.

7. *Terchloride of gold* produces in solutions of protochloride of tin and in solutions of salts of protoxide of tin mixed with hydrochloric acid a precipitate which varies in color between brown, reddish brown, and purple-red, according to the presence of more or less bichloride of tin and the state of concentration (compare § 126, 7). In very dilute solutions a more or less brown or red coloration merely is produced.

8. Solution of *chloride of mercury,* added in excess, to solutions of protochloride or of protoxide of tin mixed with hydrochloric acid, produces a white precipitate of SUBCHLORIDE OF MERCURY, owing to the protosalt of tin withdrawing from the chloride of mercury half of its chlorine.

9. If a fluid containing protoxide or protochloride of tin and hydrochloric acid is added to a mixture of *ferricyanide of potassium* and *sesqui-*

*chloride of iron* a precipitate of PRUSSIAN BLUE separates immediately, owing to the reduction of the ferricyanide ($Fe_2Cfdy$) to ferrocyanide ($Fe_4Cfy_3$). $Fe_4Cfy_3$* + 2 H Cl + 2 Sn Cl = $Fe_4Cfy_3$ + $H_3Cfy$ + 2 Sn $Cl_4$. This reaction is extremely delicate, but it can be held to be decisive only in cases where no other reducing agent is present.

10. *Zinc* precipitates from solutions mixed with hydrochloric acid METALLIC TIN in the form of gray laminæ or of a spongy mass. If the experiment is made in a platinum capsule, the latter is not colored black.

11. If compounds of protoxide of tin, mixed with *carbonate of soda* and some *borax*, or better still, with a mixture of equal parts of *carbonate of soda* and *cyanide of potassium*, are exposed on a charcoal support to the *inner blowpipe flame* malleable grains of METALLIC TIN are obtained. The best way of making quite sure of the real nature of these grains is to triturate them and the surrounding parts of charcoal with water in a small mortar, pressing heavily upon the mass; then to wash the charcoal off from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support the latter becomes covered with a coating of white binoxide. The stick of charcoal (p. 24) is also admirably adapted for the reduction of tin.

12. If to a borax bead colored slightly blue by copper a trace of a compound of tin is added and the bead is heated in the *lower reducing flame* of the gas lamp (p. 23), it will become reddish-brown to ruby-red in consequence of the reduction of the oxide of copper to suboxide (compare § 120, 14). A compound of tin is essential to this reaction.

## § 130.

### *b.* BINOXIDE OF TIN ($Sn O_2$).

1. BINOXIDE OF TIN is a powder varying in color from white to straw-yellow, and which upon heating transiently assumes a brown tint. It forms two different series of compounds with acids, bases, and water. The hydrate precipitated by alkalies from solution of bichloride of tin dissolves readily in hydrochloric acid; whilst that formed by the action of nitric acid upon tin—hydrate of metastannic acid—remains undissolved. But if it is boiled for some time with hydrochloric acid it takes up acid; if the excess of the acid is then poured off, and water added, a clear solution is obtained. The aqueous solution of the common bichloride of tin is not precipitated by concentrated hydrochloric acid, whilst that acid produces in the aqueous solution of the metastannic chloride a white precipitate of the latter compound. The solution of the common bichloride of tin is not colored yellow by addition of protochloride of tin, as is the case in a remarkable degree if the solution contains metastannic chloride (LÖWENTHAL). The dilute solutions of both chlorides of tin give upon boiling precipitates of the hydrates corresponding to the chlorides.

2. The SALTS OF BINOXIDE OF TIN are colorless. The soluble salts are decomposed at a red heat; in the neutral state they redden litmus-paper. Bichloride of tin is a volatile liquid, strongly fuming in the air.

3. *Hydrosulphuric acid* throws down from all acid and neutral solu-

* $2 Fe_2Cfdy = Fe_4Cfy_3$; for $Cfdy = C_{12}N_6Fe_2 = 2 Cfy$.

tions, particularly upon heating, a white flocculent precipitate if the solution of the binoxide is in excess; a dull yellow precipitate if the hydrosulphuric acid is in excess. The former may safely be assumed, in the case of a solution of bichloride of tin, to consist of a mixture of bichloride and bisulphide of tin (it has not however as yet been analysed); the latter consists of hydrated BISULPHIDE OF TIN. Alkaline solutions are not precipitated by hydrosulphuric acid. Presence of a very large quantity of hydrochloric acid may prevent precipitation. The bisulphide of tin dissolves readily in potassa or soda, alkaline sulphides, and concentrated boiling hydrochloric acid, as also in aqua regia. It dissolves with some difficulty in ammonia, is nearly insoluble in carbonate of ammonia, and insoluble in bisulphite of potassa. Concentrated nitric acid converts it into insoluble hydrate of metastannic acid. Upon deflagrating bisulphide of tin with nitrate and carbonate of soda sulphate of soda and binoxide of tin are obtained. If a solution of bisulphide of tin in potassa is boiled with teroxide of bismuth tersulphide of bismuth and binoxide of tin are formed, which latter substance remains dissolved in the potassa.

4. *Sulphide of ammonium* produces the same precipitate of hydrated BISULPHIDE OF TIN; the precipitate redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphide of tin unaltered.

5. *Potassa, soda,* and *ammonia, carbonate of soda* and *carbonate of ammonia* produce white precipitates which, according to the nature of the solutions, consist of hydrate of binoxide of tin, or of hydrate of metastannic acid. The former readily dissolves in a slight excess of potassa, slightly in a large excess; on the other hand it dissolves only after considerable dilution in a slight excess of soda, and on addition of more soda almost all the binoxide separates again. The latter is hardly soluble in excess of potassa or soda.

6. *Sulphate of soda* or *nitrate of ammonia* (in fact, most neutral salts of the alkalies), when added in excess, throw down from solutions of both modifications of binoxide of tin, provided they are not too acid, the whole of the tin as HYDRATED BINOXIDE OR HYDRATED METASTANNIC ACID. Heating promotes the precipitation: $Sn\,Cl_2 + 4\,(Na\,O, S\,O_3) + 4\,H\,O = Sn\,O_2, 2\,H\,O + 2\,Na\,Cl + 2\,(Na\,O, H\,O, 2\,S\,O_3)$.

7. *Metallic zinc* precipitates from solutions of bichloride of tin, in the presence of free acid, METALLIC TIN in the shape of small gray scales, or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference between tin and antimony).

8. The compounds of the binoxide of tin show the same reactions before the blowpipe or in the gas flame as those of the protoxide. Binoxide of tin is also readily reduced when fused with cyanide of potassium in a glass tube or in a crucible.

## § 131.

### *c.* TEROXIDE OF ANTIMONY ($Sb\,O_3$).

1. METALLIC ANTIMONY has a bluish tin-white color and is lustrous; it is hard, brittle, readily fusible, volatile at a very high temperature. When heated on charcoal before the blowpipe it emits thick white

fumes of teroxide of antimony, which form a coating on the charcoal; this combustion continues for some time even after the removal of the metal from the flame; it is the most distinctly visible if a current of air is directed with the blowpipe directly upon the sample on the charcoal. But if the sample on the support is kept steady, that the fumes may ascend straight, the metallic bead becomes surrounded with a net of brilliant acicular crystals of teroxide of antimony. Nitric acid oxidizes antimony readily: the dilute acid converts it almost entirely into teroxide, the more concentrated the acid the more antimonic acid is formed, boiling concentrated acid converts it almost completely into antimonic acid. Neither of the two oxides is altogether insoluble in nitric acid; traces of antimony are therefore always found in the acid fluid filtered from the precipitate. Hydrochloric acid, even boiling, does not attack antimony. In nitrohydrochloric acid the metal dissolves readily. The solution contains terchloride or pentachloride according to the degree of concentration of the acid and the duration of the action.

2. According to the different modes of its preparation, TEROXIDE OF ANTIMONY occurs either in the form of white and brilliant crystalline needles, or as a white powder. It fuses at a moderate red heat in a closed vessel; when exposed to a higher temperature it volatilizes without decomposition. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. No separation of iodine takes place on boiling it with hydrochloric acid (free from chlorine) and iodide of potassium (free from iodic acid). BUNSEN. Teroxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

3. ANTIMONIC ACID ($Sb O_2$) is pale yellow; its hydrates are white. Both the acid and its hydrates redden moist litmus-paper; they are only very sparingly soluble in water, and almost insoluble in nitric acid, but dissolve pretty readily in hot concentrated hydrochloric acid: the solution contains pentachloride of antimony and turns turbid upon addition of water. On boiling antimonic acid with hydrochloric acid and iodide of potassium iodine separates, which dissolves in the hydriodic acid present to a brown fluid (BUNSEN). Upon ignition antimonic acid loses oxygen, and is converted into infusible ANTIMONATE OF TEROXIDE OF ANTIMONY ($Sb O_2$, $Sb O_3$). Of the antimonates the potassa and ammonia salts are almost the only ones soluble in water: acids precipitate hydrate of antimonic acid from the solutions, chloride of sodium throws down from them antimonate of soda (§ 90, 2).

4. The greater part of the SALTS OF TEROXIDE OF ANTIMONY are decomposed upon ignition; the haloid salts volatilize readily and unaltered. The soluble neutral salts of antimony redden litmus-paper. With a large quantity of water they give insoluble basic salts and acid solutions containing teroxide of antimony. Thus, for instance, *water* throws down from solutions of terchloride of antimony in hydrochloric acid a white bulky precipitate of BASIC TERCHLORIDE OF ANTIMONY (powder of Algaroth), $Sb Cl_3$, $5 Sb O_3$, which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and therefore prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the basic terchloride of antimony is distinguished from the basic salts of bismuth formed under similar circumstances.

5. *Hydrosulphuric acid* precipitates from acid solutions (if the quantity of free mineral acid present is not too large), the whole of the metal as

orange-red amorphous TERSULPHIDE OF ANTIMONY. In alkaline solutions this reagent fails to produce a precipitate or, at least, it precipitates them only imperfectly; neutral solutions also are only imperfectly thrown down by it. The tersulphide of antimony produced is readily dissolved by potassa and by alkaline sulphides, especially if the latter contain an excess of sulphur; it is but sparingly soluble in ammonia, and, if free from pentasulphide of antimony, almost insoluble in bicarbonate of ammonia. It is insoluble in dilute acids, as also in acid sulphite of potassa. Concentrated boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid gas. By heating in the air it is converted into a mixture of antimonate of teroxide of antimony with tersulphide of antimony. By deflagration with nitrate of soda it gives sulphate and antimonate of soda. If a potassa solution of tersulphide of antimony is boiled with teroxide of bismuth tersulphide of bismuth precipitates, and teroxide of antimony dissolved in potassa remains in the solution. On fusing tersulphide of antimony with cyanide of potassium metallic antimony and sulphocyanide of potassium are produced. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbonic acid gas (see § 132, 12), no sublimate of antimony is produced. But if a mixture of tersulphide of antimony with carbonate of soda or with cyanide of potassium and carbonate of soda is heated in a glass tube in a stream of hydrogen gas (compare § 132, 4), a mirror of antimony is deposited in the tube, immediately behind the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid sulphuretted hydrogen throws down pentasulphide of antimony mixed with tersulphide and sulphur. The precipitate dissolves readily when heated with solution of soda or ammonia, and equally so in concentrated boiling hydrochloric acid, with evolution of hydrosulphuric acid gas and separation of sulphur, but dissolves only very sparingly in cold bicarbonate of ammonia.

6. *Sulphide of ammonium* produces in solutions of teroxide of antimony an orange-red precipitate of TERSULPHIDE OF ANTIMONY, which readily redissolves in an excess of the precipitant if the latter contains an excess of sulphur. Acids throw down from this solution pentasulphide of antimony. However, the orange color appears in that case usually of a lighter tint, owing to an admixture of free sulphur.

7. *Potassa, soda, ammonia, carbonate of soda* and *carbonate of ammonia* throw down from solutions of terchloride of antimony, and also of simple salts of teroxide of antimony,—but far less completely, and mostly only after some time, from solutions of tartar emetic or analogous compounds —a white bulky precipitate of TEROXIDE OF ANTIMONY, which redissolves pretty readily in an excess of potassa or soda, but requires the application of heat for its re-solution in carbonate of soda, and is almost insoluble in ammonia.

8. *Metallic zinc* precipitates from all solutions of teroxide of antimony, if they contain no free nitric acid, METALLIC ANTIMONY as a black powder. If a few drops of a solution of antimony, containing some free hydrochloric acid, are put into a platinum capsule (the lid of a platinum crucible), and a fragment of zinc is introduced, hydrogen containing antimonetted hydrogen is evolved and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions: this reaction I can recom-

mend as being equally delicate and characteristic. Cold hydrochloric acid fails to remove the stain, heating with nitric acid removes it immediately.

9. If a solution of teroxide of antimony in solution of potassa or soda is mixed with solution of *nitrate of silver*, a deep black precipitate of SUBOXIDE OF SILVER forms with the grayish-brown precipitate of oxide of silver. Upon now adding ammonia in excess the oxide is redissolved, whilst the suboxide is left undissolved (H. ROSE). The formation of the suboxide of silver in this process is explained as follows: $KO, SbO_5 + 4AgO = KO, SbO_5 + 2Ag_2O$. This exceedingly delicate reaction affords more especially also an excellent means of detecting teroxide of antimony in presence of antimonic acid.

10. If a solution of teroxide of antimony is introduced into a flask in which hydrogen gas is being evolved from pure *zinc* and diluted *sulphuric acid* the zinc oxidizes not only at the expense of the oxygen of the water, but also at the expense of that of the teroxide of antimony. Antimony separates accordingly in the metallic state; but a portion of the metal combines in the moment of its separation with hydrogen, forming ANTIMONETTED HYDROGEN GAS ($SbH_3$). If this operation is conducted in a gas-evolution flask, connected by means of a perforated cork with a bent tube ending in a jet,* and the hydrogen passing through the jet is ignited after the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating and burning in the flame. White fumes of teroxide of antimony rise from the flame, which condense readily upon cold substances, and are not dissolved by water. But if a cold body, such as a porcelain dish (which answers the purpose best), is now depressed upon the flame, METALLIC ANTIMONY is deposited upon the surface in a state of the most minute division, forming a deep black and almost lustreless spot. If the middle part of the tube through which the gas is passing is heated to redness the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part.

As the acids of arsenic give under the same circumstances similar stains of metallic arsenic, it is always necessary to carefully examine the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With stains deposited on a porcelain dish the object in view is most readily attained by treating them with a solution of chloride of soda (a compound of hypochlorite of soda with chloride of sodium, prepared by mixing a solution of chloride of lime with carbonate of soda in excess, and filtering); which will immediately dissolve arsenical stains, leaving those proceeding from antimony untouched, or, at least, removing them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it whilst the current of hydrogen gas still continues to pass through the tube: if the mirror volatilizes only at a higher temperature, and the hydrogen gas then issuing from the tube does not smell of garlic; if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing

* In accurate experiments it is advisable to use MARSH'S apparatus (§ 132, 10). By the employment of a platinum jet the color of the flame will be rendered very distinct.

fuses to small lustrous globules distinctly discernible through a magnifying glass,—the presence of antimony may be considered certain. Or the metals may be distinguished with great certainty by conducting through the tube a *very slow* stream of dry hydrosulphuric acid gas, and heating the mirror, proceeding in an opposite direction to that of the current. The antimonial mirror is by this means converted into tersulphide of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas is now transmitted through the glass tube, the tersulphide of antimony, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker it takes a short time to dissipate it. The reason for this is, that the tersulphide of antimony decomposes readily with hydrochloric acid, and the terchloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water the presence of antimony in the latter fluid may readily be proved by means of hydrosulphuric acid. By this combination of reactions antimony may be distinguished with positive certainty from all other metals. The reaction which hydrogen gas containing antimonetted hydrogen shows with solution of nitrate of silver and with solid potassa will be found in § 134, 6.

11. If a mixture of a compound of antimony with *carbonate of soda* and *cyanide of potassium* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognised by the peculiar reactions that mark their oxidation (compare § 131, 1).

12. In the upper reducing flame of the gas lamp (p. 23) compounds of antimony give a greenish-gray color, and no odor. The *metallic incrustation* is black, sometimes dull, sometimes bright. The *incrustation of oxide* is white. When moistened with neutral nitrate of silver, and then blown on with ammonia, it gives a black spot of antimonate of suboxide of silver (BUNSEN).

## § 132.

### *d.* ARSENIOUS ACID ($As O_3$).

1. METALLIC ARSENIC has a blackish-gray color and high metallic lustre, which it retains in dry air, but loses in moist air, becoming covered with suboxide; the metallic arsenic of commerce looks therefore rather dull, with a dim bronze lustre on the planes of crystallization. Arsenic is not very hard, but very brittle: at a dull red heat it volatilizes without fusion. The fumes have a most characteristic odor of garlic, which is ascribed to the suboxide of arsenic formed. Heated with free access of air arsenic burns—at an intense heat with a bluish flame—emitting white fumes of arsenious acid, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end the greater part of it volatilizes unoxidized, and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror); a very thin coating of the sublimate appears of a brownish-black color. In contact with air and water arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat, into arsenious acid, which dissolves only sparingly in an excess of the acid; strong nitric acid converts it

partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid; concentrated boiling sulphuric acid oxidizes it to arsenious acid, with evolution of sulphurous acid.

2. ARSENIOUS ACID generally presents the appearance either of a transparent vitreous or of a white porcelain-like mass. By trituration it gives a heavy, white, gritty powder. When heated it volatilizes in white inodorous fumes. If the operation is conducted in a glass tube a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious acid is only difficultly moistened by water; it comports itself in this respect like a fatty substance. It is sparingly soluble in cold, but more readily in hot water. It is copiously dissolved by hydrochloric acid, as well as by solution of soda and potassa. Upon boiling with nitrohydrochloric acid it dissolves to arsenic acid. It is highly poisonous.

3. The ARSENITES are mostly decomposed upon ignition either into arsenates and metallic arsenic, which volatilizes, or into arsenious acid and the base with which it was combined. Of the arsenites those only with alkaline bases are soluble in water. The insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Anhydrous terchloride of arsenic is a colorless volatile liquid, fuming in the air, which will bear the addition of a little water, but is decomposed by a larger amount into arsenious acid, which partly separates, and hydrochloric acid, which retains the rest of the arsenious acid in solution. If a solution of arsenious acid in hydrochloric acid is evaporated by heat, chloride of arsenic escapes along with the hydrochloric acid.

4. *Hydrosulphuric acid* colors aqueous solutions of arsenious acid yellow, but produces no precipitate in them; it fails equally to precipitate aqueous solutions of neutral arsenites of the alkalies; but upon addition of a strong acid a bright yellow precipitate of TERSULPHIDE OF ARSENIC forms at once. The same precipitate forms in like manner in the hydrochloric acid solution of arsenites insoluble in water. Even a large excess of hydrochloric acid does not prevent complete precipitation. Alkaline solutions are not precipitated. The precipitate is readily and completely dissolved by alkalies, alkaline carbonates and bicarbonates, and also by alkaline sulphides; but it is nearly insoluble in hydrochloric acid, even though concentrated and boiling. Boiling nitric acid decomposes and dissolves the precipitate readily.

If recently precipitated tersulphide of arsenic is digested with sulphurous acid and acid sulphite of potassa the precipitate is dissolved; upon heating the solution to boiling the fluid turns turbid, owing to the separation of sulphur, which upon continued boiling is for the greater part redissolved. The fluid contains, after expulsion of the sulphurous acid, arsenite and hyposulphite of potassa: $2\,As\,S_3 + 8\,(K\,O, 2\,S\,O_2) = 2\,(K\,O, As\,O_3) + 6\,(K\,O, S_2O_2) + S_3 + 7\,S\,O_2$ (BUNSEN).

The deflagration of tersulphide of arsenic with carbonate and nitrate of soda gives rise to the formation of arsenate and sulphate of soda. If a solution of tersulphide of arsenic in potassa is boiled with hydrated carbonate or basic nitrate of teroxide of bismuth tersulphide of bismuth and arsenite of potassa are produced.

If a mixture of tersulphide of arsenic with from 3 to 4 parts of carbonate of soda, made into a paste with some water, is spread over small glass splinters, and these, after being well dried, are rapidly heated to redness in a glass tube through which dry hydrogen gas is transmitted,

a large portion of the arsenic present is reduced to the metallic state and expelled if the temperature applied is sufficiently high. Part of the reduced arsenic forms a metallic mirror in the tube, the remainder is carried away suspended in the hydrogen gas; the minute particles of arsenic impart a bluish tint to the flame when the gas is kindled, and form stains of arsenic upon the surface of a porcelain dish depressed upon the flame. The fusion of the mixture of tersulphide of arsenic with carbonate of soda first gives rise to the formation of a double tersulphide of arsenic and sulphide of sodium, and of arsenite of soda [$2\,As_2S_3 + 4\,(Na_2O, CO_2) = 3\,Na_2S, As_2S_3 + Na_2O, As_2O_3 + 4\,CO_2$]. Upon heating these products the arsenite of soda is resolved into arsenic and arsenate of soda ($5\,As_2O_3 = 2\,As + 3\,As_2O_5$), and the tersulphide of arsenic and sulphide of sodium into arsenic and pentasulphide of arsenic and sulphide of sodium ($5\,AsS_3 = 2\,As + 3\,AsS_5$); and by the action of the hydrogen the arsenate of soda is also converted into hydrate of soda, arsenic, and water. The whole of the arsenic is accordingly expelled, except that portion of the metal which constitutes a component part of the double pentasulphide of arsenic and sulphide of sodium formed in the process, a sulphur salt which is not decomposed by hydrogen (H. Rose). This method of reduction gives indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of certainty, nor to detect arsenic in presence of antimony. (Compare § 131, 5.) The operation is conducted in the apparatus illustrated by fig. 36. *a* is the evolution flask, *b* a tube con-

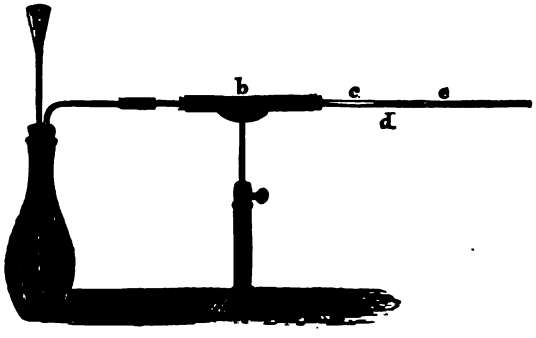


Fig. 36.

taining chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the mixture is placed; this tube is made of difficultly fusible glass free from lead. When the apparatus is completely filled with hydrogen *d* is exposed to a very gentle heat at first, in order to expel all the moisture which may still be present, and then suddenly to a very intense heat,* to prevent the sublimation of undecomposed tersulphide of arsenic. The metallic mirror is deposited near the point *e*. —Another method of effecting the reduction of tersulphide of arsenic to the metallic state, which combines with the very highest degree of delicacy the advantage of precluding the possibility of confounding arsenic with antimony, will be found described in 12 (p. 158).

* The flame of the gas-lamp with chimney, or of the blowpipe, answers the purpose best.

5. *Sulphide of ammonium* also causes the formation of TERSULPHIDE OF ARSENIC. In neutral and alkaline solutions, however, the tersulphide does not precipitate, but remains dissolved as a double sulphide of arsenic and ammonium. From this solution it precipitates immediately upon the addition of a free acid.

6. *Nitrate of silver* leaves aqueous solutions of arsenious acid perfectly clear, or at least produces only a trifling yellowish-white turbidity in them; but if a little ammonia is added a yellow precipitate of ARSENITE OF SILVER ($3\,Ag\,O, As\,O_3$) separates. The same precipitate forms of course immediately upon the addition of nitrate of silver to the solution of a neutral arsenite. The precipitate dissolves readily in nitric acid as well as in ammonia, and is not insoluble in nitrate of ammonia; if therefore a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the nitrate of ammonia formed. If an ammoniacal solution of arsenite of silver is heated to boiling, METALLIC SILVER separates, the arsenious acid being converted into arsenic acid.

7. *Sulphate of copper* produces under the same circumstances as the nitrate of silver a yellowish-green precipitate of ARSENITE OF COPPER.

8. If to a solution of arsenious acid in an excess of solution of soda or potassa, or to a solution of an alkaline arsenite mixed with *potassa* or *soda*, a few drops of a dilute solution of *sulphate of copper* are added, a clear blue fluid is obtained, which upon boiling deposits a red precipitate of SUBOXIDE OF COPPER, leaving arsenate of potassa in solution. This reaction is exceedingly delicate, provided not too much of the solution of sulphate of copper be used. Even should the red precipitate be so exceedingly minute as to escape detection on looking across the tube, yet it will always be discernible with great distinctness upon looking down the test-tube. Of course this reaction, although really of great importance in certain instances as a confirmatory proof of the presence of arsenious acid, and more particularly also as a means of distinguishing that acid from arsenic acid, is yet entirely inapplicable for the direct detection of arsenic, since grape sugar and other organic substances also produce suboxide of copper from salts of oxide of copper in the same manner.

9. If a solution of arsenious acid mixed with hydrochloric acid is heated with a perfectly clean slip of *copper* or copper wire, an iron-gray metallic film is deposited on the copper, even in highly dilute solutions; when this film increases in thickness it peels off in black scales. If the coated copper, after washing off the free acid, is heated with solution of ammonia the film peels off from the copper, and separates in form of minute spangles (REINSCH). Let it be borne in mind that these are not pure arsenic, but consist of an ARSENIDE OF COPPER ($Cu_4As$). If the substance, either simply dried or oxidized by ignition in a current of air (which is attended with escape of some arsenious acid), is heated in a current of hydrogen, there escapes relatively but little arsenic, alloys richer in copper being left behind (FRESENIUS, LIPPERT). It is only after the presence of arsenic in the alloy has been fully demonstrated that this reaction can be considered a decisive proof of the presence of that metal, as antimony and other metals will under the same circumstances also precipitate in a similar manner upon copper.

10. If an acid or neutral solution of arsenious acid or any of its

compounds is mixed with *zinc*, *water*, and *dilute sulphuric acid* ARSENETTED HYDROGEN ($AsH_3$) is formed, in the same manner as compounds of antimony give under analogous circumstances antimonetted hydrogen. (Compare § 131, 10.) This reaction affords us a most delicate test for the detection of even the most minute quantities of arsenic. The operation is conducted in the apparatus illustrated by fig. 37, or in one of similar construction.* *a* is the evolution flask, *b* a

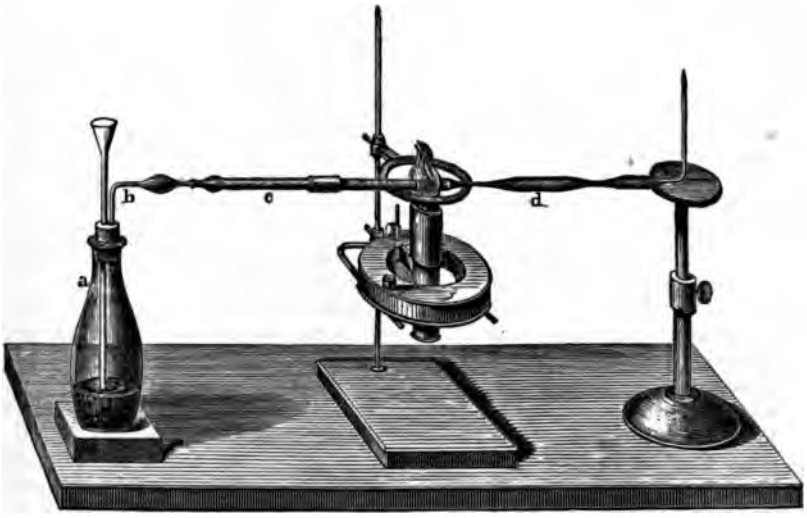


Fig. 37.

bulb intended to receive the water carried with the gaseous current, *c* a tube filled with cotton wool and small lumps of chloride of calcium for drying the gas. This tube is connected with *b* and *d* by india-rubber tubes which have been boiled in solution of soda; *d* should have an inner diameter of 7 mm. (fig. 38), and must be made of difficultly fusible glass free from lead. In experiments requiring great accuracy the tube should be drawn out as shown in fig. 37. The operation is now commenced by evolving in *a* a moderate and uniform current of hydrogen gas, from pure granulated zinc and pure sulphuric acid diluted with 3 parts of water. Addition of a few drops of bichloride of platinum will be found useful. When the evolution of hydrogen has proceeded for some time, so that it may safely be concluded the air has been completely expelled from the apparatus, the gas is kindled at the open end of the tube *d*. It is advisable to wrap a piece of cloth round the flask before kindling the gas, to guard against accidents in case of an explosion. It is now absolutely necessary first to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is done by depressing a porcelain dish horizontally upon the flame to make it spread over the surface: if the hydrogen contains arsenetted hydrogen brownish or brownish-black stains of arsenic will

Fig. 38.

* I use the very convenient form of MARSH'S apparatus recommended by OTTO in *his excellent* Lehrbuch der Chemie.

appear on the porcelain; the non-appearance of such stains may be considered as a proof of the freedom of the zinc and sulphuric acid from arsenic. In very accurate experiments, however, additional evidence is required to ensure the positive certainty of the purity of the reagents employed; for this purpose the part of the tube *d* shown in fig. 37 over the flame is heated to redness with a Berzelius or gas-lamp, and kept some time in a state of ignition: if no arsenical coating makes its appearance in the narrowed part of the tube the agents employed may be pronounced free from arsenic, and the operation proceeded with, by pouring the fluid to be tested for arsenic through the funnel tube into the flask, and afterwards some water to rinse the tube. Only a very little of the fluid ought to be poured in at first, as in cases where the quantity of arsenic present is considerable, and a somewhat large supply of the fluid is poured into the flask, the evolution of gas often proceeds with such violence as to stop the further progress of the experiment.

Now if the fluid contains an oxygen compound of arsenic or arsenic in combination with a salt radical, there is immediately evolved, along with the hydrogen, arsenetted hydrogen, which at once imparts a bluish tint to the flame of the kindled gas, owing to the combustion of the particles of arsenic separating from the arsenetted hydrogen. At the same time white fumes of arsenious acid arise, which condense upon cold objects. If a porcelain plate is now depressed upon the flame the separated and not yet reoxidized arsenic condenses upon the plate in black stains, in a similar manner to antimony. (See § 131, 10.) The stains formed by arsenic incline, however, more to a blackish-brown tint, and show a bright metallic lustre; whilst the antimonial stains are of a deep black color and but feebly lustrous. The arsenical stains may be distinguished moreover from the antimonial stains by solution of chloride of soda—hypochlorite of soda with chloride of sodium—(compare § 131, 10), which will at once dissolve arsenical stains, leaving antimonial stains unaffected, or removing them only after a considerable time.

If the heat of a Berzelius or gas-lamp is now applied to the part of the tube *d* shown in fig. 37 over the flame, a brilliant arsenical mirror makes its appearance in the narrowed portion of the tube behind the heated part; this mirror is of a darker and less silvery-white hue than that produced by antimony under similar circumstances; from which it is moreover distinguished by the facility with which it may be dissipated in a current of hydrogen gas without previous fusion, and by the characteristic odor of garlic emitted by the escaping (unkindled) gas. If the gas is kindled whilst the mirror in the tube is being heated the flame will, even with a very slight current of gas, deposit arsenical stains on a porcelain plate.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic with positive certainty in presence of antimony. In cases of this kind the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic:—

Heat the long tube through which the gas to be tested is passing to redness in several parts, to produce distinct metallic mirrors; then transmit through the tube a very weak stream of dry hydrosulphuric acid gas, and heat the metallic mirrors proceeding from the outer towards the inner border. If arsenic alone is present yellow tersulphide

of arsenic is formed inside the tube; if antimony alone is present an orange-red or black tersulphide of antimony is produced; and if the mirror consisted of both metals the two sulphides appear side by side, the sulphide of arsenic as the more volatile lying invariably before the sulphide of antimony. If you now transmit through the tube containing the sulphide of arsenic or the sulphide of antimony, or both sulphides together, dry hydrochloric gas, without applying heat, no alteration will take place if sulphide of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time. If sulphide of antimony alone is present this will entirely disappear, as already stated, § 131, 10, and if both sulphides are present the sulphide of antimony will immediately volatilize, whilst the yellow sulphide of arsenic will remain. If a small quantity of ammonia is now drawn into the tube the sulphide of arsenic is dissolved, and may thus be readily distinguished from sulphur which may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

The reaction of hydrogen containing arsenetted hydrogen with solution of nitrate of silver will be found in § 134, 6.

MARSH was the first who suggested the method of detecting arsenic by the production of arsenetted hydrogen.

11. If a small lump of arsenious acid (*a*) be introduced into the pointed end of a drawn-out glass tube (fig. 39), a fragment of quite

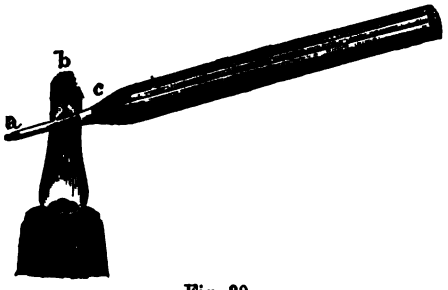


Fig. 39.

recently burnt charcoal (*b*) pushed down the tube to within a short distance of the arsenious acid, and first the charcoal then the arsenious acid heated to redness, a MIRROR OF METALLIC ARSENIC will form at *c*, owing to the reduction of the arsenious acid vapour by the red-hot charcoal. If the tube be now cut between *b* and *c* and then heated in an inclined position, with the cut end *c* turned upwards, the metallic mirror will volatilize, emitting the characteristic odor of garlic. This is both the simplest and safest way of detecting pure arsenious acid.

12. If arsenites, or arsenious acid, or tersulphide of arsenic are fused with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium* the whole of the arsenic is reduced to the metallic state, and so is the base also, if easily reducible; the eliminated oxygen converting part of the cyanide of potassium into cyanate of potassa. In the reduction of tersulphide of arsenic sulphocyanide of potassium is formed. The operation is conducted as follows:—Introduce the perfectly dry

arsenical compound into the bulb of a small bulb-tube (fig. 40), and cover it with six times the quantity of a perfectly dry mixture of equal parts of carbonate of soda and of cyanide of potassium. The whole quan-

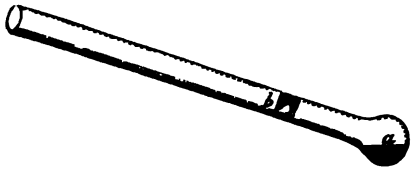


Fig. 40.

tity must not much more than half-fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Heat the bulb now gently; should some water still escape, wipe the inside of the tube perfectly dry with a twisted slip of blotting paper. It is of the highest importance for the success of the experiment to bestow great care upon expelling the water, drying the mixture, and wiping the tube clean and dry. Apply now a strong heat to the bulb, to effect the reduction of the arsenical compound, and continue this for some time, as the arsenic often requires some time for its complete sublimation. The mirror which is deposited at *b* is of exceeding purity. It is obtained from all arsenites whose bases remain either altogether unaffected, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the

Fig. 41.

simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by it, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior in simplicity and accuracy to all other methods hitherto suggested. The delicacy of the reaction may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by L. v. BABO and myself has shown that the most accurate and satisfactory results are obtained in the following manner. Figs. 41 and 42 show the apparatus in which the process is conducted. *a* is a bottle for the evolution of carbonic acid. At the bottom is a layer of plaster of Paris. While the plaster is setting the bottle should be placed in a slanting position, so that the surface of the plaster may slope towards *d*; and before the plaster is quite hard a conical hole should be scooped out of it at *d*. On the plaster bottom lumps of marble are placed. *b* is firmly fixed on *a* by means of two perforated india-rubber stoppers, or preferably by means of one long stopper tapering from the middle towards both ends. *b* is connected with *a* by the glass tube *e*, which is provided with the arrangement represented at *f* constructed of glass tubes of as large bore as possible. To the glass tube *g* is attached a short piece of india-rubber tube which reaches into the cavity in the bottom of the bottle. Water and hydrochloric acid are poured in through *h*, which is afterwards closed by a stopper containing a glass tube. On opening *i* the acid passes into the evolution bottle and the carbonic acid begins to be formed. On closing *i* the pressure of carbonic acid drives the hydrochloric acid back into *b*, and the evolution ceases. The carbonic acid is dried in *k*, which contains concentrated sulphuric acid. It then passes into the reducing tube

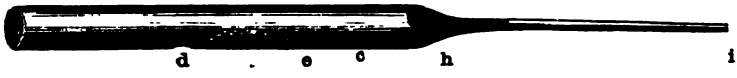


Fig. 42.

*m*, which is represented in fig. 42 half its real size; it should have a bore of 8 mm.

When the apparatus is full of carbonic acid triturate the perfectly dry sulphide of arsenic or arsenite in a slightly heated mortar with about twelve parts of a well-dried mixture consisting of three parts of carbonate of soda and one part of cyanide of potassium. The mixture must of course be quite free from arsenic (§ 46). Put the powder upon a narrow slip of card paper, bent into the shape of a gutter, and push this into the reduction-tube down to *e*; turn the tube now half-way round its axis, which will cause the mixture to drop into the tube between *e* and *d*, every other part remaining perfectly clean. Connect the tube now with the gas-evolution apparatus, and pass through it a moderate stream of carbonic acid. Heat the tube in its whole length very gently until the mixture in it is quite dry. When every trace of water is expelled, reduce the gas stream so that the single bubbles pass through the sulphuric acid at intervals of one second, and heat the reduction tube to redness at *c* (fig. 42). When *c* is red-hot, apply the flame of a second lamp to the mixture, proceeding from *d* to *e*, until the

whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *h*, whilst a small portion only escapes through *i*, imparting to the air a garlic odor. Advance the flame of the second lamp slowly and gradually up to *c*, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven to *h*. When you have effected this, close the tube at the point *i* by fusion, and apply heat, proceeding from *i* towards *h*, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner perfectly distinct mirrors of arsenic may be produced from ·0002 grm. of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, or from any other compound of antimony.

13. If arsenious acid or one of its compounds is exposed on charcoal to the reducing *flame of the blowpipe* a highly characteristic garlic odor is emitted, more especially if some carbonate of soda is added. This odor has its origin in the reduction and re-oxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the mere indications of the sense of smell, cannot be implicitly relied on.

## § 133.

### *e.* Arsenic Acid ($AsO_5$).

1. Hydrated arsenic acid crystallizes in clear prisms of the formula $2(3HO, AsO_5) + aq.$, which deliquesce in the air. The water of crystallization escapes at 100°; at a higher temperature the water of hydration escapes and the acid fuses. On strong ignition it splits into oxygen and arsenious acid. The anhydrous acid dissolves but slowly in water. Arsenic acid is poisonous.

2. Most of the arsenates are insoluble in water. Of the so-called neutral arsenates those with alkaline bases alone are soluble in water. Most of the neutral and basic arsenates can bear a strong red heat without suffering decomposition. The acid arsenates lose their excess of acid upon ignition, which passes off in the form of arsenious acid and oxygen. A solution of arsenic acid or of an arsenate in hydrochloric acid may be boiled for a long time without losing chloride of arsenic, provided too much hydrochloric acid is not present. But when the residual fluid contains about half its volume of hydrochloric acid of specific gravity 1·12, traces of terchloride of arsenic begin to escape with the hydrochloric acid.

3. *Hydrosulphuric acid* fails to precipitate alkaline and neutral solutions; but in acidified solutions it causes first reduction of the arsenic acid to arsenious acid, with separation of sulphur, then precipitation of tersulphide of arsenic. This process continues until the whole of the arsenic is thrown down as $As_2S_3$, mixed with 2 S (Wackenroder, Ludwig, H. Rose). The action never takes place immediately, and in dilute solutions frequently only after the lapse of a considerable time (twelve to twenty-four hours, for instance). Heating (to about 70°) greatly accelerates the action. If a solution of arsenic acid, or of an arsenate, is mixed with sulphurous acid, or with sulphite of soda and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; application of heat

promotes the change. If hydrosulphuric acid is now added, the whole of the arsenic is immediately thrown down as tersulphide.

4. *Sulphide of ammonium* converts the arsenic acid in neutral and alkaline solutions of arsenates into pentasulphide of arsenic, which remains in solution as a salt of pentasulphide of arsenic and sulphide of ammonium. Upon the addition of an acid to the solution this salt is decomposed, and pentasulphide of arsenic precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arsenates are precipitated with hydrosulphuric acid. It is promoted by heat. The precipitate formed is $As S_5$, and not a mixture of $As S_3$ with $S_2$.

5. *Nitrate of silver* produces under the circumstances stated § 132, 6, a highly characteristic reddish-brown precipitate of ARSENATE OF SILVER ($3 AgO, AsO_5$), which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in nitrate of ammonia. Accordingly, if a little of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to reproduce the precipitate. The ammoniacal solution of arsenate of silver does not deposit silver upon boiling (difference between arsenic and arsenious acids).

6. *Sulphate of copper* produces under the circumstances stated § 132, 7, a greenish-blue precipitate of ARSENATE OF COPPER ($2 CuO, HO, AsO_5$).

7. If a dilute solution of arsenic acid mixed with some hydrochloric acid is heated with a clean slip of *copper* the metal remains perfectly clean (WERTHER, REINSCH); but if to one volume of the solution two volumes of concentrated hydrochloric acid are added, a gray film is deposited on the copper, as in the case of arsenious acid. The reaction is under these circumstances equally delicate as with arsenious acid (REINSCH).

8. With *zinc* in presence of sulphuric acid, with *cyanide of potassium*, and before the *blowpipe*, the compounds of arsenic acid comport themselves in the same way as those of arsenious acid. If the reduction of arsenic acid by zinc is effected in a platinum capsule, the platinum does not turn black (difference from antimony).

9. If a solution of arsenic acid, or of an arsenate soluble in water, is added to a clear mixture of *sulphate of magnesia*, *chloride of ammonium*, and a sufficient quantity of *ammonia*, a crystalline precipitate of ARSENATE OF AMMONIA AND MAGNESIA ($2 MgO, NH_4O, AsO_5 + 12 aq.$) separates; from concentrated solutions immediately, from dilute solutions after some time. If a small portion of the precipitate is dissolved on a watch-glass in a drop of nitric acid, a little nitrate of silver added, and the solution touched with a glass rod dipped in ammonia, brownish-red arsenate of silver is formed. Or if a small portion of the precipitate is dissolved in hydrochloric acid and hydrosulphuric acid is passed into the solution with warming, a yellow precipitate is formed. (Differences between arsenate and phosphate of magnesia and ammonia.)

## § 134.

*Recapitulation and remarks.*—I will here describe first the different ways adapted to effect the detection or separation of tin, antimony, and arsenic, when present together, and afterwards the means of *distinguishing* between the several oxides of the three metals.

1. If you have a mixture of sulphide of tin, sulphide of antimony, and sulphide of arsenic, triturate 1 part of it with 1 part of dry carbonate of soda and 1 part of nitrate of soda, and transfer the mixed powder gradually to a small porcelain crucible containing 2 parts of nitrate of soda kept in a state of fusion at a not over-strong heat; oxidation of the sulphides ensues, attended with slight deflagration. The fused mass contains binoxide of tin, arsenate and antimonate of soda, with sulphate, carbonate, nitrate, and nitrite of soda. You must take care not to raise the heat to such a degree, nor continue the fusion so long, as to lead to a reduction of the nitrite of soda to the caustic state, that there may not be formed stannate of soda soluble in water. Upon treating the mass with a little cold water binoxide of tin and antimonate of soda remain undissolved, whilst arsenate of soda and the other salts are dissolved. If the filtrate is acidified with nitric acid, and heat is applied to remove carbonic and nitrous acids, the arsenic acid may be detected and separated, either with nitrate of silver, according to § 133, 5, or with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, according to § 133, 9.

If the undissolved residue, consisting of binoxide of tin and antimonate of soda, is, after being washed once with cold water and three times with dilute spirits of wine, treated with some hydrochloric acid in the lid of a platinum crucible, and a gentle heat applied, the mass is either completely dissolved or, if the tin is present in a large proportion, a white residue is left undissolved. If, regardless of the presence of this latter, a fragment of zinc is added, the compounds are reduced to the metallic state, when the antimony will at once reveal its presence by blackening the platinum. If, after the evolution of hydrogen has nearly stopped, the remainder of the zinc is taken away, and the contents of the lid are heated with some hydrochloric acid, the tin dissolves to protochloride, whilst the antimony is left undissolved in the form of black flakes. The tin may then be more distinctly tested in the solution, with chloride of mercury, or with a mixture of sesquichloride of iron and ferricyanide of potassium, and the antimony, after solution in a little aqua regia, with hydrosulphuric acid. As this method of detecting arsenic, tin, and antimony in presence of each other is adopted in the systematic course of analysis, I have here simply explained the principle upon which it is based, and refer for the details of the process to § 192.

2. If the mixed sulphides, after being freed from the greater part of the adhering water, by laying the filter containing them on blotting paper, are treated with fuming hydrochloric acid, with application of a gentle heat, the sulphides of antimony und tin dissolve, whilst the sulphide of arsenic is left almost completely undissolved. By treating this with ammonia, and evaporating the solution obtained, with addition of a small quantity of carbonate of soda, an arsenical mirror may easily be produced from the residue, by means of cyanide of potassium and carbonate of soda in a stream of carbonic acid gas (§ 132, 12). The solution, which contains the tin and the antimony, may be treated as stated in 1.

If a great excess of antimony is present the latter solution may also be mixed with sesquicarbonate of ammonia in excess, and boiled; when a large proportion of the antimony will dissolve, leaving binoxide of tin behind, mixed with but little teroxide of antimony; in which undissolved

residue the tin may now be the more readily detected by the method described in 1 (BLOXAM).

3. If the mixed sulphides are digested at a gentle heat with some common solid carbonate of ammonia and water sulphide of arsenic dissolves, whilst the sulphides of antimony and tin remain undissolved. But even this separation is not quite absolute, as traces of sulphide of antimony are apt to pass into the solution, whilst some sulphide of arsenic remains in the residue. The sulphide of arsenic precipitating from the alkaline solution upon acidifying this latter with hydrochloric acid must therefore, especially if consisting only of a few flakes, after washing, be treated with ammonia, the solution evaporated, with addition of a small quantity of carbonate of soda, and the residue fused with cyanide of potassium in a stream of carbonic acid, to make quite sure by the production of an arsenical mirror. The residue, insoluble in carbonate of ammonia, should be treated as directed in 2.

4. If sulphide of antimony, sulphide of tin, and sulphide of arsenic are dissolved in sulphide of potassium, a *large* excess of a concentrated solution of sulphurous acid added, the mixture digested for some time on the water-bath, boiled until all sulphurous acid is expelled, then filtered, the filtrate contains all the arsenic as arsenious acid (which may be precipitated from it by hydrosulphuric acid), whilst tersulphide of antimony and bisulphide of tin are left behind undissolved (BUNSEN). These latter may then be treated as directed in 2.

5. In the analysis of alloys, binoxide of tin, teroxide of antimony, and arsenic acid are often obtained together as a residue insoluble in nitric acid. The best way is to fuse this residue with hydrate of soda in a silver crucible, to treat the mass with water, and add one-third (by volume) of spirit of wine; then to filter the fluid off from the antimonate of soda, which remains undissolved, and wash the latter with spirit of wine mixed with a few drops of solution of carbonate of soda. In the presence of much tin it is advisable to repeat the above treatment on the residue, in order to extract all the tin. The filtrate is acidified with hydrochloric acid, and the tin and arsenic are then precipitated as sulphides, with the aid of heat. On heating the precipitated sulphides in a stream of hydrosulphuric acid gas the whole of the tin is left as sulphide, whilst the sulphide of arsenic volatilizes, and may be received in solution of ammonia (H. ROSE).

6. For the method of separating antimony and arsenic, and distinguishing between the two metals, by treating with hydrosulphuric acid the mirror produced by MARSH'S process, and separating the resulting sulphides by means of hydrochloric acid gas, I refer to § 132, 10. Antimony and arsenic may, however, when mixed together in form of hydrogen compounds, be separated also in the following ways. *a.* Conduct the gases mixed with an excess of hydrogen, first through a tube containing glass splinters moistened with solution of acetate of lead, to retain the hydrochloric and hydrosulphuric gases, then in a slow stream into a solution of nitrate of silver. Almost all the antimony in the gas falls down as black antimonide of silver ($Ag_3Sb$), whilst the arsenic passes into the solution as arsenious acid, with reduction of the silver, and may be detected in the fluid as arsenite of silver, by cautious addition of ammonia, or—after precipitating the excess of silver by hydrochloric acid—by means of hydrosulphuric acid. Since, however, *a little* antimony always passes into the solution, the hydrosul-

phuric acid precipitate must not be put down as sulphide of arsenic without further examination, according to § 132, 12. In the precipitated antimonide of silver, which is often mixed with much silver, the antimony may be most readily detected, by heating the precipitate—thoroughly freed from arsenious acid by boiling with water—with tartaric acid and water to boiling. This will dissolve the antimony alone, which may then be readily detected by means of hydrosulphuric acid in the solution acidified with hydrochloric acid (A. W. HOFMANN). *b.* Conduct the gases mixed with an excess of hydrogen through a rather wide glass tube, 3 or 4 inches of which are filled with caustic potassa in small lumps. The potassa decomposes the antimonetted hydrogen entirely becoming coated with a lustrous film of metal. The arsenetted hydrogen is on the contrary not decomposed, and may be detected readily on its exit from the tube by the production of the arsenical mirror (§ 132, 10) or by its action on solution of nitrate of silver (DRAGENDORFF).

7. *Protoxide* and *binoxide of tin* may be detected in presence of each other, by testing one portion of the solution for the protoxide with chloride of mercury, terchloride of gold or a mixture of ferricyanide of potassium and sesquichloride of iron, and another portion for the binoxide, by pouring it into a concentrated hot solution of sulphate of soda. For the last test the solution must not contain much free acid.

8. *Teroxide of antimony* in presence of *antimonic acid* may be identified by the reaction described in § 131, 9. *Antimonic acid* in presence of *teroxide of antimony*, by heating the oxide, which must be free from other bodies, with hydrochloric acid and iodide of potassium (§ 131, 2 and 3).

9. *Arsenious acid* and *arsenic acid* in the same solution may be distinguished by means of nitrate of silver. If the precipitate contains little arsenate and much arsenite of silver it is necessary, in order to identify the former, to add cautiously and drop by drop most highly dilute nitric acid, which dissolves the yellow arsenite of silver first. A still safer way to detect small quantities of arsenic acid in presence of arsenious acid is to precipitate the solution with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia (§ 132, 9), by which means an actual separation of the two acids is effected. Arsenious acid may be recognised in presence of arsenic acid by the immediate precipitation of the acidified solution with hydrosulphuric acid in the cold; also by the reduction of oxide of copper in alkaline solution; also by the separation of metallic silver by boiling the ammoniacal solution of the silver salts. To ascertain the degree of sulphuration of a sulphide of arsenic in a sulphur salt, boil the alkaline solution of the salt under examination with hydrate of teroxide of bismuth, filter off from the tersulphide of bismuth formed, and test the filtrate for arsenious and arsenic acids. To distinguish between the ter- and pentasulphide of arsenic, extract first the sulphur which may be present by means of sulphide of carbon, then dissolve the residue in ammonia, add nitrate of silver in excess, filter off the sulphide of silver, and observe whether arsenite or arsenate of silver is formed upon addition of ammonia.

*Special Reactions of the rarer Oxides of the Sixth Group.*

§ 135.

*a.* Oxide of Iridium.

Iridium is found in combination with platinum and other metals in platinum ores, also, and more especially, as a native alloy of osmium and iridium. Alloyed with platinum, it has of late been employed for crucibles, &c. Iridium resembles platinum, but it is brittle; it fuses with extreme difficulty. In the compact state, or reduced at a red heat by hydrogen, it dissolves in no acid, not even in aqua regia (difference between iridium and gold and platinum); reduced in the moist way, say by formic acid, or largely alloyed with platinum, it dissolves in aqua regia to bichloride. *Acid sulphate of potassa* in a state of fusion will oxidize, but not dissolve it (difference between iridium and rhodium). It oxidizes by fusion with *hydrate of soda*, with access of air, or by fusion with nitrate of soda. The compound of sesquioxide of iridium with soda, which is formed in this process, dissolves partially in water; by heating with aqua regia it gives a deep-black solution of bichloride of iridium and chloride of sodium.

If iridium powder is mixed with chloride of sodium, the mixture heated to incipient redness, and treated with *chlorine gas*, sodio-bichloride of iridium is formed, which dissolves in water to a deep reddish-brown fluid. *Potassa*, added in excess, colors the solutions greenish, a little brownish-black potassio-bichloride of iridium precipitating at the same time. If the solution is heated, and exposed some time to the air, it acquires at first a reddish tint, which changes afterwards to azure blue (characteristic difference between iridium and platinum); if the solution is now evaporated to dryness, and the residue treated with water, a colorless fluid is obtained, with a blue deposit of binoxide of iridium left undissolved. *Hydrosulphuric acid* in the first place decolorizes solutions of bichloride of iridium, protochloride is formed, with separation of sulphur, and finally brown sulphide of iridium precipitates. *Sulphide of ammonium* produces the same precipitate, which redissolves readily in an excess of the precipitant. *Chloride of potassium* precipitates potassio-bichloride of iridium as a dark-brown powder, insoluble in a concentrated solution of chloride of potassium. *Chloride of ammonium* precipitates from concentrated solutions ammonio-bichloride of iridium in the form of a dark-red powder, consisting of microscopic octahedrons, insoluble in concentrated solution of chloride of ammonium. This double-salt (and also the corresponding potassium compound), especially when in hot solution, is turned olive-green by *nitrite of potassa*, owing to the formation of a double salt of the sesquichloride of iridium [$2\,(K\,Cl, Ir\,Cl_2) + K\,O, N\,O_3 = 3\,K\,Cl, Ir_2\,Cl_3 + N\,O_4$]; this double salt crystallizes out on cooling. On heating or evaporating the green solution with an excess of nitrite of potassa it turns yellow, and when boiled deposits a white precipitate which is hardly soluble in water and hydrochloric acid. (This reaction may be taken advantage of to separate iridium from platinum, Gibbs.) If the ammonio-bichloride of iridium is dissolved in water by boiling, and *oxalic acid* is added, a reduction of the bichloride to sesquichloride takes place, and on this account the solution remains clear on cooling (here iridium differs from platinum, C. Lea). If *protochloride of tin* is added to bichloride of iridium and the solution is boiled, and then excess of potassa is added and the mixture is boiled again, a leather-colored precipitate is formed. *Sulphate of iron* decolorizes the solution, but does not produce a precipitate. *Zinc* precipitates black metallic iridium. On suspending binoxide of iridium in a solution of *nitrite of potassa*, saturating with *sulphurous acid* and boiling with renewal of the evaporating water till all the free sulphurous acid is expelled, the whole of the iridium is converted into insoluble sulphite of binoxide (any binoxide of platinum which may be present will remain dissolved as sulphite of protoxide of platinum and potassa, C. Birnbaum). Ignited with *carbonate of soda* in the upper oxidizing flame compounds of iridium yield the metal, which when elutriated out is gray, devoid of lustre, and without ductility.

*b.* Oxides of Molybdenum.

Molybdenum is not largely disseminated in nature, and is found only in moderate quantities, more especially as sulphide of molybdenum and as molybdate of lead (yellow lead ore). Since the use of molybdate of ammonia as a means of detecting and determining phosphoric acid, molybdenum has acquired considerable importance in practical chemistry. Molybdenum is tin-white and hard, when heated in the air it oxidizes, it is soluble in nitric acid and very difficult to fuse. The protoxide and sesquioxide are black, the binoxide is dark-brown. When heated in the air or treated with nitric

acid the metal and oxides are all converted into MOLYBDIC ACID ($MoO_3$). The latter is a white porous mass, which in water separates into fine scales, and dissolves to a slight extent; it fuses at a red heat, in close vessels it volatilizes only at a very high temperature, in the air it volatilizes easily at a red heat and sublimes to transparent laminæ and needles. On igniting it in a current of hydrogen it is first converted into the binoxide, and afterwards by strong and long-continued heating into the metal. The non-ignited molybdic acid dissolves in acids. The solutions are colorless; the hydrochloric solution is colored by contact with zinc soon, on addition of protochloride of tin immediately; the color being brown, green or blue according to the proportion of reducing agent and the concentration of the fluid. Digested with *copper* the sulphuric acid solution turns blue, the hydrochloric acid solution brown. The reaction often requires some time. *Ferrocyanide of potassium* produces a reddish-brown precipitate, *infusion of galls* a green precipitate. *Hydrosulphuric acid*, added in small proportion, imparts a blue tint to the solutions of molybdic acid; added in larger proportion it produces a brownish-black precipitate; the fluid over the latter at first appears green. But after being allowed to stand for some time, and heated, additional quantities of hydrosulphuric acid being repeatedly conducted into it, the whole of the molybdenum present will ultimately though slowly separate as brownish-black tersulphide of molybdenum. The precipitated tersulphide of molybdenum dissolves in sulphides of the alkali metals; acids precipitate from the sulphur salts the sulphur acid ($MoS_3$), application of heat promotes the separation. By heating to redness in the air, or by heating with nitric acid, sulphide of molybdenum is converted into molybdic acid. If a solution of molybdic acid in excess of ammonia is mixed with yellow sulphide of ammonium, and boiled for some time, a dark-red liquid of great depth of color is formed in addition to the brownish-black precipitate, unless a very large excess of sulphide of ammonium is present. Sulphocyanide of potassium, if added to a solution of molybdic acid containing hydrochloric acid, produces no color until zinc is added, when the fluid becomes crimson; the coloration is due to the formation of a sulphocyanide of molybdenum corresponding to the binoxide or sesquioxide. Phosphoric acid does not destroy the color (difference from sulphocyanide of iron). On shaking the red fluid with ether, the latter becomes colored (C. D. BRAUN).

Molybdic acid dissolves readily in solutions of *pure alkalies* and *carbonates of the alkalies;* from concentrated solutions *nitric acid* or *hydrochloric acid* throws down molybdic acid, which redissolves in a large excess of the precipitant. The solutions of molybdates of the alkalies are colored yellow by *hydrosulphuric acid*, and give afterwards, upon addition of acids, a brownish-black precipitate. For the deportment of molybdic acid with *phosphoric acid* and ammonia, see § 142, 10.

Molybdic acid volatilizes when heated on charcoal in the *oxidizing flame*, coating the charcoal with a yellow, often crystalline, powder, which turns white on cooling. In the *reducing flame* the acid suffers reduction to the metallic state, the molybdenum is obtained as a gray powder by elutriating the charcoal support. Sulphide of molybdenum gives in the oxidizing flame sulphurous acid and an incrustation of molybdic acid on the charcoal.

### c. OXIDES OF TUNGSTEN.

This metal most commonly occurs in nature in the forms of tungstate of lime and of a double tungstate of protoxide of iron and protoxide of manganese called wolfram. Obtained by the reduction of tungstic acid in a current of hydrogen at an intense red heat, it is an iron-gray powder, very difficultly fusible. This powder is converted by ignition in the air into tungstic acid ($WO_3$); by ignition in a current of dry air-free chlorine into dark violet terchloride which sublimes, and a more volatile red compound ($WCl_5$, $WCl_6$). These chlorides are decomposed by water into the corresponding hydrated oxides and hydrochloric acid. Tungsten is insoluble or scarcely soluble in acids, even in aqua regia, and also in potassa; it dissolves, however, in the latter if mixed with chloride of soda. BINOXIDE OF TUNGSTEN is black; by intense ignition with free access of air it is converted into tungstic acid. TUNGSTIC ACID is lemon-yellow, fixed, insoluble in water and acids. By fusing tungstic acid with acid sulphate of potassa, and treating the fused mass with water, an acid solution is obtained, which contains no tungstic acid; after the removal of this solution the residue, consisting of tungstate of potassa and a large excess of tungstic acid, completely dissolves in water containing carbonate of ammonia (means of separating tungstic from silicic acid). Tungstates of the alkalies soluble in water are formed readily by fusion with alkaline carbonates, but with difficulty by boiling with solution of the same. *Hydrochloric acid, nitric acid,* and *sulphuric acid* produce in the solution of these tungstates white precipitates, which turn yellow on boiling and are insoluble in an excess of the acids (difference from molybdic acid), but soluble in ammonia. Upon

evaporating with an excess of hydrochloric acid to dryness, and treating the residue with water, the tungstic acid is left undissolved. *Chloride of barium, chloride of calcium, acetate of lead, nitrate of silver, nitrate of suboxide of mercury* produce white precipitates. *Ferrocyanide of potassium*, with addition of some acid, colors the fluid deep brownish-red, and after some time produces a precipitate of the same color. *Tincture of galls*, with a little acid added, produces a brown precipitate. *Hydrosulphuric acid* barely precipitates acid solutions. *Sulphide of ammonium* fails to precipitate solutions of tungstates of alkalies; upon acidifying the mixture light-brown tersulphide of tungsten precipitates, which is slightly soluble in pure water, but insoluble in water containing salts. *Protochloride of tin* produces a yellow precipitate; on acidifying with hydrochloric acid, and applying heat, this precipitate acquires a beautiful blue color (highly delicate and characteristic reaction). If solutions of tungstates of alkalies are mixed with hydrochloric acid, or, better still, with an excess of phosphoric acid, and *zinc* is added, the fluid acquires a beautiful blue color. *Phosphate of soda and ammonia* dissolves tungstic acid. The bead, exposed to the oxidizing flame, appears clear, varying from colorless to yellowish; in the reducing flame it acquires a pure blue color, and upon addition of sulphate of protoxide of iron a blood-red color. By mixing with a little *carbonate of soda*, and exposing in the cavity of the charcoal support to the reducing flame, tungsten in powder is obtained, which may be separated by elutriation. The tungstates which are insoluble in water may, most of them, be decomposed by digestion with acids. Wolfram, which strongly resists the action of acid, is fused with carbonated alkali, when water will dissolve out of the fused mass the tungstate of alkali formed.

### *d.* Oxides of Tellurium.

Tellurium is not widely disseminated, and is found in small quantities only in the native state, or alloyed with other metals, or as tellurous acid. It is a white brittle, but readily fusible metal, which may be sublimed in a glass tube. Heated in the air it burns with a greenish-blue flame, emitting thick white fumes of tellurous acid. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid to tellurous acid ($TeO_2$). Tellurium in powder dissolves in cold concentrated sulphuric acid to a purple-coloured fluid, from which it separates again upon addition of water. Tellurous acid is white; at a gentle red heat it fuses to a yellow fluid; it is volatilized by strong ignition in the air, forming no crystalline sublimate. The anhydrous acid dissolves readily in hydrochloric acid, sparingly in nitric acid, freely in solution of potassa, slowly in ammonia, barely in water. The hydrate of tellurous acid is white; it is perceptibly soluble in cold water, and dissolves in hydrochloric acid and in nitric acid. By addition of water white hydrate is thrown down from the solution, and from the nitric acid solution nearly the whole of the tellurous acid separates after some time as a crystalline precipitate, even without addition of water. *Pure alkalies* and *carbonates of the alkalies* throw down from the hydrochloric acid solution white hydrate, which is soluble in an excess of the precipitant. *Hydrosulphuric acid* produces in acid solutions a brown precipitate ($TeS_2$, in color like protosulphide of tin), which dissolves very freely in sulphide of ammonium. *Sulphite of soda, protochloride of tin*, and *zinc* precipitate black metallic tellurium. Telluric acid ($TeO_3$) is formed by fusing tellurium or tellurites with nitrates and carbonates of the alkalies. The fused mass is soluble in water. The solution remains clear upon acidifying with hydrochloric acid in the cold; but upon boiling chlorine is disengaged, and tellurous acid formed, and the solution is therefore now precipitated by water if the excess of acid is not too great. If tellurium, its sulphide, or an oxygen compound of the metal is fused with *cyanide of potassium* in a stream of hydrogen, a cyanide of tellurium and potassium is formed. The fused mass dissolves in water, but a current of air throws down from the solution the whole of the tellurium (difference and means of separating tellurium from selenium). When tested in the dry way by Bunsen's method (p. 23) the compounds of tellurium give a grayish-blue color in the upper reducing flame, while at the same time the upper oxidizing flame appears green. The volatilization is unaccompanied by any odor. The *incrustation produced by reduction* is black, with a blackish-brown edge, and gives a crimson solution when heated with concentrated sulphuric acid. The *incrustation of oxide* is white, scarcely visible; protochloride of tin colors it black, metallic tellurium being separated. When heated with *carbonate of soda* in the *stick of charcoal* compounds of tellurium yield telluride of sodium, which when placed on clean silver and moistened produces a black mark, and when treated with hydrochloric acid (in the presence of enough tellurium) gives an odor of telluretted hydrogen with separation of tellurium.

### *e.* Oxides of Selenium.

Selenium occurs in nature in the form of selenides of metals. It is found occasionally in the dust of roasting-furnaces, and also in the Nordhausen oil of vitriol. It resembles sulphur in some respects, tellurium in others. Fused selenium is grayish-black; it volatilises at a high temperature, and may be sublimed. Heated in the air it burns to selenious acid ($SeO_2$), exhaling a characteristic smell of decaying horse-radish. Concentrated sulphuric acid dissolves selenium without oxidizing it; upon diluting the solution the selenium falls down in red flakes. Nitric acid and aqua regia dissolve selenium to selenious acid. The latter is converted at 200° into a yellow gas. Sublimed anhydrous selenious acid appears in form of white four-sided needles, its hydrate in the form of crystals resembling those of nitrate of potassa. Both the acid and its hydrate dissolve readily in water to a strongly acid fluid. Of the neutral salts only those with the alkalies are soluble in water; the solutions have alkaline reactions. All selenites dissolve readily in nitric acid, with the exception of the selenites of lead and silver, which dissolve with difficulty. *Hydrosulphuric acid* produces in solutions of selenious acid or of selenites (in presence of free hydrochloric acid) a yellow precipitate of sulphide of selenium (?) which, upon heating, turns reddish-yellow, soluble in sulphide of ammonium. *Chloride of barium* produces (after neutralization of the free acid, should any be present), a white precipitate of selenite of baryta, which is soluble in hydrochloric acid and in nitric acid. *Protochloride of tin* or *sulphurous acid*, with addition of hydrochloric acid, produces a red precipitate of selenium, which turns gray at a high temperature. *Metallic copper* when placed in a warm solution of selenious acid containing hydrochloric acid becomes immediately coated black; if the fluid remains long in contact with the copper, it turns light red from separation of selenium (Reinsch). Selenic acid is formed by heating selenium or its compounds with carbonates and nitrates of the alkalies. The fused mass dissolves in water; the solution remains clear upon acidifying with hydrochloric acid; when concentrated by boiling, it evolves chlorine, whilst the selenic acid is reduced to selenious acid. By fusing selenium or its compounds with *cyanide of potassium* in a stream of hydrogen gas, a cyanide of selenium and potassium is obtained, from which the selenium is not eliminated by the action of the air (as is the case with tellurium); it separates, however, upon long continued boiling, after addition of hydrochloric acid. When tested according to p. 23, compounds of selenium give a blue *color to the flame*, and by *volatilization* and combustion of the vapor the above-mentioned odor is emitted. The *incrustation produced by reduction* is brick-red to cherry-red, and gives a dirty green solution with concentrated sulphuric acid. The *incrustation of oxide* is white, and when moistened with protochloride of tin becomes red from separated selenium. In the *charcoal stick* with *carbonate of soda* selenide of sodium is formed, which when placed on silver and moistened produces a black mark, and when treated with acids yields selenetted hydrogen.

## B.—Deportment of the Acids and their Radicals.

### § 136.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the bases, into general reagents, *i.e.*, such as indicate the group to which the acid under examination belongs; and special reagents, *i.e.*, such as serve to effect the detection and identification of the individual acids. The groups into which we classify the various acids can scarcely be defined with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those of inorganic and organic acids. We base this division upon those characteristics by which, irrespectively of theoretical considerations, the ends of analysis are most easily attained. We select therefore here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and call organic those acids of which the salts—

(particularly those which have an alkali or an alkaline earth for base) —are decomposed upon ignition, with separation of carbon. By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which an acid belongs. The salts of organic acids with alkalies or alkaline earths are converted into carbonates when heated gently to redness.

Before proceeding to the special study of the several acids considered in this work, I give here, as I have done with the bases, a general view of the whole of them classified in groups.

I. INORGANIC ACIDS.

FIRST GROUP:

Division *a.* *Chromic acid* (sulphurous and hyposulphurous acids, iodic acid).

Division *b.* *Sulphuric acid* (hydrofluosilicic acid).

Division *c.* *Phosphoric acid, boracic acid, oxalic acid, hydrofluoric acid* (phosphorous acid).

Division *d.* *Carbonic acid, silicic acid.*

SECOND GROUP:

*Chlorine* and *hydrochloric acid; bromine* and *hydrobromic acid; iodine* and *hydriodic acid; cyanogen* and *hydrocyanic acid*, together with *hydroferro-* and *hydroferricyanic acids; sulphur* and *hydrosulphuric acid* (nitrous acid, hypochlorous acid, chlorous acid, hypophosphorous acid).

THIRD GROUP:

*Nitric acid, chloric acid* (perchloric acid).

II. ORGANIC ACIDS.

FIRST GROUP:

*Oxalic acid, tartaric acid, citric acid, malic acid* (racemic acid).

SECOND GROUP:

*Succinic acid, benzoic acid.*

THIRD GROUP:

*Acetic acid, formic acid* (lactic acid, propionic acid, butyric acid).

The acids printed in italics are more frequently met with in the examination of minerals, waters, ashes of plants, industrial products, medicines, &c.; the others are more rarely met with.

## I. INORGANIC ACIDS.

### § 137.

*First Group.*

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY CHLORIDE OF BARIUM.

This group is again subdivided into four divisions, viz.:

1. Acids which are decomposed in acid solution by hydrosulphuric acid, and to which attention has therefore been directed already in the testing for bases, viz., CHROMIC ACID (sulphurous acid and hyposul-

phurous acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts; and also iodic acid).*

2. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta compounds of which are insoluble in hydrochloric acid: SULPHURIC ACID (hydrofluosilicic acid).
3. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta compounds of which dissolve in hydrochloric acid, apparently without decomposition, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation: PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, HYDROFLUORIC ACID (phosphorous acid). (Oxalic acid belongs more properly to the organic group. We consider it, however, here with the acids of the inorganic class, as the property of its salts to be decomposed upon ignition without actual carbonization may lead to its being overlooked as an organic acid.)
4. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta salts of which are soluble in hydrochloric acid with separation of the acid: CARBONIC ACID, SILICIC ACID.

*First Division of the First Group of the Inorganic Acids.*

## § 138.

### CHROMIC ACID ($CrO_3$).

1. CHROMIC ACID appears as a scarlet crystalline mass, or in the form of distinct acicular crystals. Upon ignition it is resolved into sesquioxide of chromium and oxygen. It deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-yellow tint, which remains visible in very dilute solutions.

2. The CHROMATES are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition. Those with alkaline bases are soluble in water, and when neutral are fixed; the solutions of the neutral alkaline chromates are yellow, those of the alkaline bichromates are reddish-yellow. These tints are visible in highly dilute solutions. The yellow color of the solution of a neutral salt changes to reddish-yellow on the addition of an acid, owing to the formation of an acid chromate.

3. *Hydrosulphuric acid* acting upon the acidified solution produces first a brownish coloration of the fluid, then a green coloration, arising from the salt of sesquioxide of chromium formed; this change of color is attended with separation of sulphur, which imparts a milky appearance to the fluid [$KO, 2CrO_3 + 4(HO, SO_2) + 3HS = KO, SO_3 + Cr_2O_3, 3SO_2 + 7HO + 3S$]. Heat promotes this reaction, part of the sulphur being in that case converted into sulphuric acid.

4. *Sulphide of ammonium*, when added in excess to a solution of an

* To this first division of the first group of inorganic acids belong properly also all the oxygen compounds of a distinctly pronounced acid character, which have been discussed already with the Sixth Group of the metallic oxides (acids of arsenic, antimony, selenium, &c.). But as the reaction of these compounds with hydrosulphuric acid tends to lead to confounding them rather with other metallic oxides than with other acids, it appeared the safer course to class these compounds, which may be said to stand between the bases and the acids, with the metallic oxides.

acid chromate of an alkali, immediately produces a bluish-gray-green precipitate of hydrated CHROMATE OF SESQUIOXIDE OF CHROMIUM; on boiling the whole of the chromium separates as green hydrated oxide. In a solution of neutral chromate of potassa at first a dark brownish coloration alone is produced, but the bluish-gray-green precipitate above mentioned soon separates.

5. Chromic acid may also be reduced to sesquioxide by means of many other substances, and more particularly by *sulphurous acid*, by heating with concentrated *hydrochloric acid*, or with the dilute acid and alcohol (in which case chloride of ethyl and aldehyde are evolved), by *metallic zinc*, by heating with *tartaric acid*, *oxalic acid*, &c. All these reactions are clearly characterized by the change of the red or yellow color of the solution to the green or violet tint of the salt of sesquioxide of chromium.

6. *Chloride of barium* produces in aqueous solutions of chromates a yellowish-white precipitate of CHROMATE OF BARYTA ($BaO, CrO_3$), soluble in dilute hydrochloric and nitric acids.

7. *Nitrate of silver* produces in aqueous solutions of chromates a dark purple-red precipitate of CHROMATE OF SILVER ($AgO, CrO_3$) soluble in nitric acid and in ammonia; in slightly acid solutions it produces a precipitate of BICHROMATE OF SILVER ($AgO, 2CrO_3$).

8. *Acetate of lead* produces in an aqueous or acetic acid solution of a chromate a yellow precipitate of CHROMATE OF LEAD ($PbO, CrO_3$), soluble in potassa, sparingly soluble in dilute nitric acid, insoluble in acetic acid. Upon heating with alkalies the yellow neutral salt is converted into basic red chromate of lead ($2PbO, CrO_3$).

9. If a very dilute acid solution of *peroxide of hydrogen** (about 6 or 8 c.c.) is covered with a layer of ether (about half a centimetre thick), and a fluid containing chromic acid is added, the solution of peroxide of hydrogen acquires a fine blue color. By inverting the test-tube, closed with the thumb, repeatedly, without much shaking, the solution becomes colorless, whilst the ether acquires a blue color. The latter reaction is particularly characteristic. One part of chromate of potassa in 40,000 parts of water suffices to produce it distinctly (STOREB); presence of vanadic acid materially impairs the delicacy of the test (WERTHER).† The blue coloration is in all probability caused by a combination of chromic acid with peroxide of hydrogen. After some time reduction of the chromic acid to sesquioxide takes place, and at the same time decoloration of the ether.

10. If insoluble chromates are fused with *carbonate* and *nitrate of soda*, and the fused mass is treated with water, the fluid obtained appears yellow from the alkaline chromate which it holds in solution; upon the addition of an acid the yellow colour changes to reddish-yellow. The oxides are left either in the pure state or as carbonates, unless they are soluble in the caustic soda formed from the nitrate.

* Solution of peroxide of hydrogen may be easily prepared by triturating a fragment of peroxide of barium (about the size of a pea) with some water, and adding it with stirring to a mixture of about 30 c.c. hydrochloric acid, and 120 c.c. water. The solution keeps a long time without suffering decomposition. In default of peroxide of barium, impure peroxide of sodium may be used instead, which is obtained by heating a fragment of sodium in a porcelain capsule until it takes fire, and letting it burn.

† *Journ. f. prakt. Chem.* 83, 195.

11. The compounds of chromic acid show the same reactions with *phosphate of soda and ammonia* and with *borax* in the blowpipe flame, as the compounds of sesquioxide of chromium.

12. Very minute quantities of chromic acid may be detected by one of the following methods: *a.* mix with the fluid, slightly acidified with sulphuric acid, a little tincture of guaiacum (1 part of the resin to 100 parts of alcohol of 60 per cent.) when an intense blue coloration of the fluid will at once make its appearance, speedily vanishing again, however, where mere traces of chromic acid are present (H. SCHIFF); *b.* mix the solution of the alkaline chromate, which must be as neutral as possible with some dilute decoction of logwood, when a very intense black coloration will be produced; in the presence of exceedingly small quantities of chromic acid the color is violet-red (R. WILDENSTEIN).

Chromic acid being reduced by hydrosulphuric acid to sesquioxide of chromium, this acid is in the course of analysis always found in the examination for bases. The intense color of the solutions containing chromic acid, the excellent reaction with peroxide of hydrogen, and the characteristic precipitates produced by solutions of salts of lead and salts of silver, afford moreover ready means for its detection. For the discovery of traces of chromium present in many minerals, for instance in serpentine, the reactions in 12 may be used after the mineral has been fused with alkaline carbonate and nitrate.

### *Rarer Acids of the First Division.*

### § 139.

### *a.* SULPHUROUS ACID ($SO_2$).

SULPHUROUS ACID is a colorless, uninflammable gas, which exhales the stifling odor of burning sulphur. It dissolves copiously in water. The solution has the odor of the gas, reddens litmus-paper, and bleaches Brazil-wood paper. It absorbs oxygen from the air, and is thereby converted into sulphuric acid. The salts are colorless. Of the neutral sulphites, those with alkaline base only are readily soluble in water; many of the sulphites insoluble or sparingly soluble in water dissolve in an aqueous solution of the sulphurous acid, but fall down again on boiling. All the sulphites evolve sulphurous acid when treated with *sulphuric acid*. *Chlorine water* dissolves most sulphites to sulphates. *Chloride of barium* precipitates neutral sulphites, but not free sulphurous acid. The precipitate dissolves in hydrochloric acid. *Hydrosulphuric acid* decomposes the free sulphurous acid, water and pentathionic acid being formed and free sulphur eliminated. If to a solution of sulphurous acid mixed with an equal volume of hydrochloric acid, a piece of clean *copper* wire is added, and the mixture is boiled, the copper appears black, as if covered with soot, if much sulphurous acid is present; but only dull if a little is present (H. REINSCH). If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from *zinc* or *aluminium* and *hydrochloric acid*, hydrosulphuric acid is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of acetate of lead to which has been added a sufficient quantity of soda to redissolve the precipitate which forms at first. Sulphurous acid is a powerful reducing agent; it reduces chromic acid, permanganic acid, chloride of mercury (to subchloride), decolorizes iodide of starch, produces a blue precipitate in a mixture of ferricyanide of potassium and sesquichloride of iron, &c. With a hydrochloric acid solution of *protochloride of tin* a yellow precipitate of BISULPHIDE OF TIN is formed after some time. If an aqueous solution of an alkaline sulphite is mixed with acetic acid just to give it an incipient acid reaction, and is then added to a relatively large amount of solution of *sulphate of zinc*, mixed with a very small quantity of *nitroprusside of sodium*, the fluid acquires a red color if the quantity of the sulphite present is not too inconsiderable, but when the quantity of the sulphite is very minute the coloration makes its appearance only after addition of some solution

of ferrocyanide of potassium. If the quantities are not altogether too minute, a purple-red precipitate will form upon the addition of the ferrocyanide of potassium (BÖDEKER). Hyposulphites of the alkalies do not show this reaction.

### *b.* HYPOSULPHUROUS ACID ($S_2O_2$).

This acid does not exist in the free state. Most of its salts are soluble in water. The solutions of most hyposulphites may be boiled without suffering decomposition; hyposulphite of lime is resolved upon boiling into sulphite of lime and sulphur. If *hydrochloric acid* or *sulphuric acid* is added to the solution of a hyposulphite, the fluid remains at first clear and inodorous, but after a short time—the shorter the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and exhales the odor of sulphurous acid. Application of heat promotes this decomposition. *Nitrate of silver* produces a white precipitate of HYPOSULPHITE OF SILVER, which is soluble in an excess of the hyposulphite; after a little while (upon heating almost immediately) this precipitate turns black, being decomposed into sulphide of silver and sulphuric acid. Hyposulphite of soda dissolves chloride of silver; upon the addition of an acid the solution remains clear at first, but after some time, and immediately upon boiling, sulphide of silver separates. *Chloride of barium* produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid. *Ferric chloride* colors the solutions of alkaline hyposulphites reddish-violet (here they differ from alkaline sulphites); on standing the liquid loses its color, especially when heated, protochloride of iron being formed. Acidified solution of *chromic acid* is immediately reduced by hyposulphites, *iodide of starch* is at once decolorized. With *zinc* or *aluminium* and *hydrochloric acid* the hyposulphites behave like the sulphites.

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Where it is required to find sulphites and hyposulphites of the alkalies in presence of alkaline sulphides, as is often the case, solution of sulphate of zinc is first added to the fluid until the sulphide is decomposed; the sulphide of zinc is then filtered off, and one part of the filtrate is tested for hyposulphurous acid by addition of acid, another portion for sulphurous acid with nitroprusside of sodium, &c.

### *c.* IODIC ACID ($IO_5$).

IODIC ACID crystallizes in white, six-sided tables; at a moderate heat it is resolved into iodine vapor and oxygen; it is readily soluble in water. The salts are decomposed upon ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and metallic oxide: the iodates with an alkaline base alone dissolve readily in water. *Chloride of barium* throws down from solution of iodates of the alkalies a white precipitate of IODATE OF BARYTA, which is soluble in nitric acid; *nitrate of silver* a white granular-crystalline precipitate of IODATE OF SILVER, which dissolves readily in ammonia, but only sparingly in nitric acid. *Hydrosulphuric acid* throws down from solutions of iodic acid IODINE, which then dissolves in hydriodic acid; the precipitation is attended with separation of sulphur. If an excess of hydrosulphuric acid is added, the fluid loses its color, and a further separation of sulphur takes place, the iodine being converted into hydriodic acid. Iodic acid combined with bases is also decomposed by hydrosulphuric acid. *Sulphurous acid* throws down IODINE, which upon addition of an excess of the acid is converted into hydriodic acid.

*Second Division of the First Group of the Inorganic Acids.*

## SULPHURIC ACID ($SO_3$).

### § 140.

1. ANHYDROUS SULPHURIC ACID is a white feathery-crystalline mass which emits strong fumes upon exposure to the air; HYDRATED SULPHURIC ACID (which contains rather more water than corresponds to the formula $HO,SO_3$) forms an oily liquid, colorless and transparent like water. Both the anhydrous and hydrated acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydrous acid with a hissing noise.

2. The neutral SULPHATES are readily soluble in water with the exception of the sulphates of baryta, strontia, lime, and lead. The basic sulphates of the oxides of the heavy metals which are insoluble in water dissolve in hydrochloric acid or in nitric acid. Most of the sulphates are colorless or white. The sulphates of the alkalies are not decomposed by ignition. The other sulphates are acted upon in different ways by a red heat, some of them being readily decomposed, others with difficulty, and some resisting decomposition altogether.

3. *Chloride of barium* produces even in exceedingly dilute solutions of sulphuric acid and of the sulphates a finely-pulverulent, heavy, white precipitate of SULPHATE OF BARYTA ($BaO, SO_3$), insoluble in dilute hydrochloric and nitric acids. From very dilute solutions the precipitate separates only after standing for some time. Concentrated acids and concentrated solutions of many salts impair the delicacy of the reaction.

4. *Acetate of lead* produces a heavy white precipitate of SULPHATE OF LEAD ($PbO, SO_3$) which is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The salts of sulphuric acid with the alkaline earths which are insoluble in water and acids are converted into CARBONATES, by fusion with *alkaline carbonates*. But the sulphate of lead is reduced to the state of OXIDE when treated in this manner. Both the conversion of the former into carbonates and the reduction of the latter to the state of oxide are attended with the formation of an alkaline sulphate. The sulphates of the alkaline earths and sulphate of lead are also resolved into insoluble carbonates and soluble alkaline sulphate by digestion or boiling with concentrated solutions of carbonates of the alkalies (comp. §§ 95, 96, 97).

6. Upon fusing sulphates with *carbonate of soda* on *charcoal* in the inner flame of the blowpipe, or heating them in the stick of charcoal (p. 24) in the lower reducing flame, the sulphuric acid is reduced, and sulphide of sodium formed, which may be readily recognised by the odor of hydrosulphuric acid emitted upon moistening the sample and the part of the charcoal into which the fused mass has penetrated, and adding some acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water and some acid, a black stain of sulphide of silver is immediately formed. (Compounds of tellurium and selenium give the same reaction.)

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*Remarks.*—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of baryta, since they redissolve immediately upon diluting the acid fluid with water. It is a rule that should never be departed from, in testing for sulphuric acid with chloride of barium, to dilute the fluid largely; a little hydrochloric acid should also be added, which counteracts the adverse influence of many salts, as, for instance, citrates of the alkalies. Where very minute quantities of sulphuric acid are to be detected the

fluid should be allowed to stand several hours at a gentle heat; the trace of sulphate of baryta formed will in that case be found deposited at the bottom of the vessel. When the least uncertainty exists about the nature of the precipitate produced by chloride of barium in presence of hydrochloric acid, the reaction in 6 will at once set all doubt at rest. In looking for very small quantities of sulphuric acid in the presence of much hydrochloric or nitric acid, the greater part of the latter should first be evaporated off or neutralized. To detect free sulphuric acid in presence of a sulphate the fluid is mixed with a very little cane-sugar, and evaporated to dryness in a porcelain dish at 100°. If free sulphuric acid was present a black residue remains, or in the case of most minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way.

### § 141.

#### Hydrofluosilicic Acid ($HF, SiF_2$).

Hydrofluosilicic acid is a very acid fluid; upon evaporation on platinum it volatilizes completely as fluoride of silicon and hydrofluoric acid. When evaporated in glass it etches the latter. With bases it forms water and silico-fluorides of the metals, which are most of them soluble in water, redden litmus-paper, and are resolved upon ignition into metallic fluorides and fluoride of silicon. *Chloride of barium* forms a crystalline precipitate with hydrofluosilicic acid (§ 95, 6). Chloride of strontium and acetate of lead form no precipitates with this acid. *Salts of potassa* precipitate transparent gelatinous SILICO-FLUORIDE OF POTASSIUM; *ammonia* in excess precipitates HYDRATED SILICIC ACID, with formation of fluoride of ammonium. By heating metallic silico-fluorides with concentrated *sulphuric acid* dense fumes are emitted in the air, arising from the evolution of hydrofluoric and silicofluoric gas. If the experiment is conducted in a platinum vessel covered with glass the fumes ETCH the glass (§ 146, 5); the residue contains the sulphates formed.

*Third Division of the First Group of the Inorganic Acids.*

### § 142.

#### *a.* Phosphoric Acid ($PO_5$).

1. Phosphorus is a colorless, transparent, solid body, of 1·84 specific gravity; it has a waxy appearance. Taken internally it acts as a virulent poison. It fuses at 44·3°, and boils at 290°. By the influence of light phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air at the common temperature, it exhales a highly characteristic and most disagreeable odor, copious fumes being evolved which are luminous in the dark. These fumes are formed by oxidation of the vapor of phosphorus, and consist of phosphoric and phosphorous acids. When the air is moist, ozone, peroxide of hydrogen and nitrite of ammonia are produced at the same time. Phosphorus very readily takes fire, burning with a luminous flame to phosphoric acid, which appears in the form of white fumes. By the protracted influence of light, or by heating to 250°, phosphorus is converted into a red variety, the so-called amorphous phosphorus. In this state it does not alter in the air, it is not luminous, its inflammability is much decreased, and it has a specific gravity of 2·1. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily upon heating. The solutions contain at first, besides phosphoric acid, also phosphorous acid. Hydro-

chloric acid does not dissolve phosphorus. If phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphuretted hydrogen gas escapes. If a substance containing unoxidized phosphorus is placed at the bottom of a flask, and a slip of paper moistened with solution of nitrate of silver is by means of a cork loosely inserted into the mouth suspended inside the flask, and a gentle heat applied (from 30° to 40°), the paper slip will turn black in consequence of the reducing action of the phosphorus fumes, even though only a most minute quantity of phosphorus should be present. If after the termination of the reaction the blackened part of the paper is boiled with water, the undecomposed portion of the silver salt precipitated with hydrochloric acid, the fluid filtered, and the filtrate evaporated as far as practicable on the water-bath, the presence of phosphoric acid in the residue may be shown by means of the reactions described below. (J. SCHERER). It must be borne in mind that the silver salt is blackened also by hydrosulphuric acid, formic acid, volatile products of putrefaction, &c.; and also that the detection of phosphoric acid in the slip of paper can be of value only where the latter and the filtering paper were perfectly free from phosphorus. As regards the deportment of phosphorus upon boiling with dilute sulphuric acid, and in a hydrogen evolution apparatus supplied with zinc and dilute sulphuric acid, see § 227.

2. Anhydrous PHOSPHORIC ACID is a white, snowlike mass, which rapidly deliquesces in the air. When treated with water it hisses like a red-hot iron, and is at first only partially dissolved, in time, however, the solution is complete. It forms with water and bases three series of compounds, viz., with three equivalents of water or base hydrate of tribasic phosphoric acid or common phosphates; with two equivalents of water or base hydrate of pyrophosphoric acid or pyrophosphates; with one equivalent of water or base hydrate of metaphosphoric acid or metaphosphates. As the meta- and pyrophosphoric acids are of comparatively rare occurrence they will be treated less fully in a supplemental paragraph.

3. The HYDRATE of TRIBASIC PHOSPHORIC ACID ($3\,H\,O, P\,O_5$) forms colorless and pellucid crystals, which deliquesce rapidly in the air to a syrupy non-caustic liquid. The action of heat changes it into hydrated meta- or pyrophosphoric acid, according as either one or two equivalents of water are expelled. Heated in an open platinum dish the hydrate of common phosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes.

4. The action of heat fails to decompose the TRIBASIC PHOSPHATES with fixed bases, but converts them into pyrophosphates if they contain one equivalent of basic water or ammonia, and into metaphosphates if they contain two equivalents. Of the tribasic phosphates those with alkaline base alone are soluble in water, in the neutral state. The solutions manifest alkaline reaction. If pyro- or metaphosphates are fused with carbonate of soda the fused mass contains the phosphoric acid invariably in the tribasic state.

5. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates of the alkalies, but not in solutions of the hydrate, a white precipitate of PHOSPHATE OF BARYTA ($2\,Ba\,O, H\,O\,P\,O_5$; or

$3\,Ba\,O, P\,O_5$),* which is soluble in hydrochloric and nitric acids, but sparingly soluble in chloride of ammonium.

6. Solution *of sulphate of lime* produces in neutral or alkaline solutions of phosphates, but not in solutions of the hydrate, a white precipitate of PHOSPHATE OF LIME ($2\,Ca\,O, H\,O, P\,O_5$ or $3\,Ca\,O, P\,O_5$), which dissolves readily in acids, even in acetic acid, and is soluble also in chloride of ammonium.

7. *Sulphate of magnesia* produces in concentrated neutral solutions of phosphates of the alkalies a white precipitate of PHOSPHATE OF MAGNESIA ($2\,Mg\,O, H\,O, P\,O_5 + 14$ aq.), which often separates only after some time; upon boiling, a precipitate of basic salt ($3\,Mg\,O, P\,O_5 + 5$ aq.) is thrown down immediately. The latter precipitate forms also upon addition of sulphate of magnesia to the solution of a basic alkaline phosphate. But if a mixture of sulphate of magnesia and ammonia with sufficient chloride of ammonium to redissolve the precipitate of hydrate of magnesia is added to a solution of free phosphoric acid or of an alkaline phosphate, a white, crystalline, and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\,Mg\,O, N\,H_4O, P\,O_5 + 12$ aq.) is formed, even in highly dilute solutions. This precipitate is insoluble in ammonia and most sparingly soluble in chloride of ammonium, but dissolves readily in acids, even in acetic acid. It makes its appearance often only after the lapse of some time; stirring promotes its separation (§ 98, 8). The reaction can be considered decisive only if no arsenic acid is present (§ 133, 9).

8. *Nitrate of silver* throws down from solutions of neutral and basic alkaline phosphates a light-yellow precipitate of PHOSPHATE OF SILVER ($3\,Ag\,O, P\,O_5$), which is readily soluble in nitric acid and in ammonia. If the solution contained a basic phosphate the fluid in which the precipitate is suspended manifests a neutral reaction; whilst the reaction is acid if the solution contained a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives, for the 3 eq. of oxide of silver which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water.

9. If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish-white, flocculent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON ($Fe_2O_3, P\,O_5 + 4$ aq.) is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; but it can be held to be decisive only if no arsenic acid is present, as this shows the same reaction. To effect the complete separation of the phosphoric acid from the alkaline earths, a sufficient quantity of sesquichloride of iron is added to impart a reddish color to the solution, which is then boiled (whereby the whole of the sesquioxide of iron is

* Precipitates of the former composition are produced in solutions containing an alkaline phosphate with two equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate with three equivalents of a fixed base or ammonia.

thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution; add carbonate of soda until the fluid is nearly neutral, then acetate of soda, and finally one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

10. If a few c. c. of the solution of *molybdate of ammonia* in nitric acid (§ 52) are poured into a test tube, and a little of a fluid is added containing phosphoric acid in neutral or acid solution, a light-yellow finely-pulverulent precipitate forms at once or after a very short time, even in the cold, if the quantity of phosphoric acid is not too inconsiderable; this precipitate speedily subsides to the bottom of the tube, or is deposited on the sides. With exceedingly minute quantities of phosphoric acid, as *e.g.* ·00002 grm., a few hours must be allowed for the manifestation of the reaction, which should be aided also by applying a gentle heat, but not higher than 40°. If no other coloring substances are present, the fluid above the precipitate appears colorless. Never allow the quantity of the fluid to be tested to exceed one-third of the quantity of the reagent, and never consider a mere yellow coloration to be a proof of phosphoric acid.

The yellow precipitate contains MOLYBDIC ACID, AMMONIA, WATER, and a little PHOSPHORIC ACID (about 3 per cent.). As it is insoluble in dilute acids only in presence of an excess of molybdic acid, addition of phosphoric acid in excess will necessarily altogether prevent its formation, which should be borne in mind. A large amount of hydrochloric acid and certain organic substances, *e.g.* tartaric acid, will impede or prevent the precipitation. The precipitate, after subsiding, may be readily recognised even in dark-colored fluids. By washing it with the solution of molybdate of ammonia with which the precipitation has been effected, dissolving in ammonia, and adding a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, phosphate of magnesia and ammonia is produced.

By conducting the operation in the manner above stated, phosphoric acid cannot well be confounded with any other acid; since arsenic acid gives in the cold no precipitate with solution of molybdate of ammonia in nitric acid, though it gives one upon application of heat, and more especially upon boiling (the fluid above this precipitate appears yellow); and silicic acid shows no reaction with it in the cold, and gives only a strong yellow coloration on heating, and no precipitate.

11. If a finely-powdered substance containing phosphoric acid (or a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of carbonate of soda, 1 part of nitrate of potassa, and 1 part of silicic acid, the mixture fused in a platinum spoon or crucible, the fused mass boiled with water, the solution obtained decanted, carbonate of ammonia added to it, the fluid boiled again, and the silicic acid which is thereby precipitated filtered off, the filtrate now holds in solution alkaline phosphate, and may accordingly be tested for phosphoric acid as directed in 7, 8, 9, or 10.

12. On igniting and pulverizing a substance containing phosphoric

acid, placing it into a tube of the thickness of a straw and sealed at one end, adding a fragment of magnesium wire about two lines long (or a small piece of sodium), which should be covered by the sample, and then heating, a vivid incandescence will be observed and phosphide of magnesium (or of sodium) will be formed. When the black contents of the tube are crushed and moistened with water they exhale the characteristic odor of phosphuretted hydrogen. (WINKELBLECH, BUNSEN.)

13. *White of egg* is not precipitated by solution of hydrate of tribasic phosphoric acid, nor by solutions of tribasic phosphates mixed with acetic acid.

§ 143.

*a. Bibasic phosphoric acid.* The solution of the hydrate $2HO, PO_5$ is converted by boiling into solution of the hydrate $3HO, PO_5$. The solutions of the salts bear heating without suffering decomposition; but upon boiling with a strong acid the phosphoric acid is converted into the tribasic state. If the salts are fused with carbonate of soda in excess tribasic phosphates are produced. Of the neutral pyrophosphates only those with alkaline bases are soluble in water; the acid salts (*e.g.*, $NaO, HO, PO_5$) are by ignition converted into metaphosphates ($NaO, PO_5$). *Chloride of barium* fails to precipitate the free acid; from solutions of the salts it precipitates white PYROPHOSPHATE OF BARYTA ($2BaO, PO_5$), soluble in hydrochloric acid. *Nitrate of silver* throws down from a solution of the hydrate, especially upon addition of an alkali, a white, earthy-looking precipitate of PYROPHOSPHATE OF SILVER ($2AgO, PO_5$), which is soluble in nitric acid and in ammonia. *Sulphate of magnesia* precipitates PYROPHOSPHATE OF MAGNESIA ($2MgO, PO_5$). The precipitate dissolves in an excess of the pyrophosphate, as well as in an excess of the sulphate of magnesia. Ammonia fails to precipitate it from these solutions. Upon boiling the solution it separates again (means of detecting pyrophosphoric acid in presence of phosphoric acid). A concentrated solution of *luteo-cobaltic chloride* added to an alkaline pyrophosphate produces an immediate precipitation of pale reddish-yellow spangles. (Here pyrophosphoric acid differs from phosphoric and metaphosphoric acids, C. D. BRAUN.) *White of egg* is not precipitated by solution of the hydrate nor by solutions of the salts mixed with acetic acid. *Molybdate of ammonia*, with addition of nitric acid, fails to produce a precipitate.

*β. Monobasic phosphoric acid.* Five sorts of monobasic phosphates are known, and the hydrates also corresponding to most of these have been produced. The several reactions by which to distinguish between these I will not enter upon here, and confine myself to the simple observation that the monobasic phosphoric acids differ from the bibasic and tribasic phosphoric acids in this, that the solutions of the hydrates of the monobasic acids precipitate *white of egg* at once, and the solutions of their salts after addition of acetic acid. Those hydrates and salts which are precipitated by *nitrate of silver* produce with that reagent a white precipitate. A mixture of *sulphate of magnesia*, chloride of ammonium, and ammonia fails to precipitate the monobasic phosphoric acids and their salts, or produces precipitates soluble in chloride of ammonium. All monobasic phosphates yield upon fusion with carbonate of soda tribasic phosphate of soda.

## § 144.

### *b.* BORACIC ACID ($BO_3$).

1. BORACIC ACID, in the anhydrous state, is a colorless, fixed glass, fusible at a red heat; hydrate of boracic acid ($HO, BO_3$) is a porous, white mass; in the crystalline state ($HO, BO_3 + 2$ aq.), it presents small scaly laminæ. It is soluble in water and in spirit of wine; upon evaporating the solutions a large proportion of boracic acid volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus-paper, and impart to turmeric-paper a faint brown-red tint, which acquires intensity upon drying. The BORATES are not decomposed upon ignition; those with alkaline bases alone are readily

soluble in water. The solutions of borates of the alkalies are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, if not too highly dilute, a white precipitate of BORATE OF BARYTA, which is soluble in acids and ammoniacal salts. The formula of this precipitate, when thrown down from solutions of neutral borates, is $BaO, BO_3 + aq.$; when thrown down from solutions of acid borates, $3\,BaO, 5\,BO_3 + 6\,aq.$ (H. ROSE).

3. *Nitrate of silver* produces in concentrated solutions of neutral borates of the alkalies a white precipitate, inclining slightly to yellow from admixture of free oxide of silver ($AgO, BO_3 + HO$); in concentrated solutions of acid borates a white precipitate of $3\,AgO, 4\,BO_3$. Dilute solutions of borates give with nitrate of silver a brown precipitate of oxide of silver (H. ROSE). All these precipitates dissolve in nitric acid and in ammonia.

4. If dilute *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot prepared solutions of alkaline borates, the BORACIC ACID separates upon cooling, in the form of shining crystalline scales.

5. If *alcohol* is poured over free boracic acid or a borate—with addition, in the latter case, of *a sufficient quantity of concentrated sulphuric acid* to liberate the boracic acid—and the alcohol is kindled, the flame appears of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture; this tint is imparted to the flame by the boracic acid which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the first flickering of the flame its borders will now appear green, even though the quantity of the boracic acid be so minute that it fails to produce a perceptible coloring of the flame when treated in the usual manner. As salts of copper also impart a green tint to the flame of alcohol, the copper which might be present must first be removed by means of hydrosulphuric acid. Presence of metallic chlorides also may lead to mistakes, as the chloride of ethyle formed in that case colors the borders of the flame bluish-green.

6. If a solution of boracic acid, or of a borate with an alkali or an alkaline earth for base, is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of *turmeric-paper* is half dipped into it, and then dried on a watch-glass at 100°, the dipped half shows a peculiar RED tint (H. ROSE).

This reaction is very delicate; care must be taken not to confound the characteristic red coloration with the blackish-brown color which turmeric-paper acquires when moistened with rather concentrated hydrochloric acid, and then dried; nor with the brownish-red coloration which sesquichloride of iron, or a hydrochloric acid solution of molybdate of ammonia or of zirconia, gives to turmeric-paper, more particularly upon drying. By moistening turmeric-paper reddened by boracic acid with a solution of an alkali or an alkaline carbonate, the color is changed to bluish-black or greenish-black; but a little hydrochloric acid will at once restore the brownish-red color (A. VOGEL, H. LUDWIG).

7. If a substance containing boracic acid is reduced to a fine powder, this with addition of a drop of water, mixed with 3 parts of a flux com-

posed of 4½ parts of bisulphate of potassa and 1 part of finely pulverized fluoride of calcium, free from boracic acid, and the paste exposed on the loop of a platinum wire in the outer mantle of the Bunsen gas flame, or at the apex of the inner flame of the blowpipe, fluoride of boron escapes, which imparts to the flame—though only for a few instants—a green tint. With readily decomposed compounds the reaction may be obtained by simply moistening the sample with hydrofluosilicic acid, and holding it in the flame.

8. Boracic acid or borates, fused with carbonate of soda on the loop of a platinum wire, give, when placed in the flame of the *spectrum apparatus*, a spectrum of four well marked lines of equal width, equidistant from each other. $B_1$ is brilliant yellowish-green (coinciding with Ba $\gamma$), $B_2$ is brilliant light-green (coinciding with Ba $\beta$), $B_3$ is pale bluish-green (nearly coinciding with the blue barium line), $B_4$ is blue, very pale, close to Sr $\delta$ (SIMMLER).

## § 145.

### *c.* OXALIC ACID ($C_4O_6 = \bar{O}$).

1. The HYDRATE OF OXALIC ACID ($2\,H\,O, C_4O_6$) is a white powder; the CRYSTALLIZED ACID ($2\,H\,O, C_4O_6 + 4$ aq.) forms colorless rhombic prisms. Both dissolve readily in water and in spirit of wine. By heating rapidly in open vessels part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating and provoke coughing. If the hydrate is heated in a test-tube part of it sublimes unaltered.

2. The whole of the OXALATES undergo decomposition at a red heat, the oxalic acid being converted into carbonic acid and carbonic oxide. The oxalates of the alkalies and of baryta, strontia, and lime are in this process converted into carbonates (if pure, and if the heat is gentle, almost without separation of charcoal). Oxalate of magnesia is converted into pure magnesia even by a very gentle red heat. The oxalates with metallic bases leave either the pure metal or the oxide behind, according to the reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of alkaline oxalates a white precipitate of OXALATE OF BARYTA ($2\,Ba\,O, C_4O_6 + 2$ aq.), which dissolves very sparingly in water, more readily in water containing chloride of ammonium, acetic acid, or oxalic acid, freely in nitric acid and in hydrochloric acid; ammonia reprecipitates it from the latter solutions unaltered.

4. *Nitrate of silver* produces in solutions of oxalic acid and of alkaline oxalates a white precipitate of OXALATE OF SILVER ($2\,Ag\,O, C_4O_6$), which is readily soluble in concentrated hot nitric acid and also in ammonia, but dissolves with difficulty in dilute nitric acid, and is most sparingly soluble in water.

5. *Lime water* and all the soluble *salts of lime*, and consequently also *solution of sulphate of lime*, produce in even highly dilute solutions of oxalic acid or of oxalates of the alkalies, white finely pulverulent precipitates of OXALATE OF LIME ($2\,Ca\,O, C_4O_6 + 2$ aq., and occasionally $2\,CaO, C_4O_6 + 6$ aq.), which dissolve readily in hydrochloric acid and in

nitric acid, but are nearly insoluble in oxalic acid and in acetic acid, and practically insoluble in water. The presence of salts of ammonia does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of free oxalic acid by salts of lime. In highly dilute solutions the precipitate is only formed after some time.

6. If hydrated oxalic acid or an oxalate, in the dry state, is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water or base, and thus causes its decomposition into CARBONIC ACID and CARBONIC OXIDE ($C_2O_4 = 2\,CO + 2\,CO_2$), the two gases escaping with effervescence. If the quantity operated upon is not too minute the carbonic oxide may be kindled; it burns with a blue flame. Should the sulphuric acid acquire a dark color in this reaction, this is a proof that the oxalic acid contained some organic substance in admixture.

7. If oxalic acid or an oxalate is mixed with finely pulverized *binoxide of manganese* (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by escaping CARBONIC ACID [$2\,MnO_2 + C_2O_4 + 2\,SO_3 = 2\,(MnO, SO_3) + 4\,CO_2$].

8. If oxalates of alkaline earths are boiled with a concentrated solution of *carbonate of soda*, and filtered, the oxalic acid is obtained in the filtrate in combination with soda, whilst the precipitate contains the base as carbonate. With oxalates containing for their base oxides of heavy metals, this operation is not always sure to attain the desired object, as many of these oxalates, *e.g.* oxalate of protoxide of nickel, will partially dissolve in the alkaline fluid, with formation of a double salt. Metals of this kind should therefore be separated as sulphides.

## § 146.

### *d.* HYDROFLUORIC ACID (HF).

1. Anhydrous HYDROFLUORIC ACID is a colorless corrosive gas, which fumes in the air, and is freely absorbed by water. Liquid hydrofluoric acid is distinguished from all other acids by the property of dissolving crystallized silicic acid, and also the silicates which are insoluble in hydrochloric acid. Hydrofluosilicic acid and water are formed in the process of solution ($SiO_2 + 3\,HF = SiF_3, HF + 2\,HO$). With metallic oxides hydrofluoric acid forms metallic fluorides and water.

2. The FLUORIDES of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkaline earths are either insoluble or very difficultly soluble in water. Fluoride of aluminium is readily soluble. Most of the fluorides of the heavy metals are very sparingly soluble in water, as the fluorides of copper, lead, and zinc; many others dissolve in water without difficulty, as the sesquifluoride of iron, protofluoride of tin, and fluoride of mercury. Many of the fluorides insoluble or difficultly soluble in water dissolve in free hydrofluoric acid; others do not. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of barium* precipitates aqueous solutions of hydrofluoric acid, but much more completely solutions of fluorides of the alkalies. The bulky white precipitate of FLUORIDE OF BARIUM (BaF) is almost

absolutely insoluble in water, but dissolves in large quantities of hydrochloric acid or nitric acid, from which solutions ammonia fails to precipitate it, or throws it down only very incompletely, owing to the dissolving action of the neutral ammonia salts.

4. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides a gelatinous precipitate of FLUORIDE OF CALCIUM (Ca F), which is so transparent as at first to induce the belief that the fluid has remained perfectly clear. Addition of ammonia promotes the complete separation of the precipitate. The precipitate is practically insoluble in water, and only very slightly soluble in hydrochloric acid and nitric acid in the cold; it dissolves somewhat more largely upon boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the salt of ammonia formed retains it in solution. Fluoride of calcium is scarcely more soluble in free hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, no matter whether soluble or insoluble, is treated in a platinum crucible with just enough *concentrated sulphuric acid* to make it into a thin paste, the crucible covered with the convex face of a watch-glass of hard glass coated with bees-wax, which has been removed again in some places by tracing lines in it with a pointed piece of wood, the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found more or less deeply ETCHED into the glass. (The coating with wax may be readily effected by heating the glass cautiously, putting a small piece of wax upon the convex face, and spreading the fused mass equally over it. The removal of the wax coating is effected by heating the glass gently, and wiping with a cloth.) If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases appear when the glass is breathed upon. This appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess. The impressions which thus appear upon breathing on the glass may, however, owe their origin to other causes; therefore, though their non-appearance may be held as a proof of the absence of fluorine, their appearance is not a positive proof of the presence of that element. At all events, they ought only to be considered of value where they can be developed again after the glass has been properly washed with water, dried, and wiped.*

This reaction fails if there is too much silicic acid present, or if the substance is not decomposed by sulphuric acid. In such cases one of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride *decomposable by sulphuric acid*,

* J. NICKLÈS states that etchings on glass may be obtained with all kinds of sulphuric acid, and, in fact, with all acids suited to effect evolution of hydrofluoric acid. I have tried watch-glasses of Bohemian glass with sulphuric and other acids, but could get no etchings in confirmation of this statement. Still, proper caution demands that before using the sulphuric acid, it should first be positively ascertained that its fumes will not etch glass. Should the sulphuric acid contain hydrofluoric acid, the latter may be easily removed by diluting with an equal volume of water and evaporating in a platinum dish to the original strength.

but mixed with a large proportion of silicic acid, the fluorine in it may be detected by heating the mixture in a test-tube with *concentrated sulphuric acid*, as FLUOSILICIC GAS is evolved in this process, which forms dense white fumes in moist air. If the gas is conducted into water through a bent tube moistened inside, the latter has its transparency more or less impaired, owing to the separation of silicic acid. If the quantity operated upon is rather considerable, hydrate of silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid.

The following process answers best for the detection of small quantities of fluorine. Heat the substance with concentrated sulphuric acid in a flask closed with a cork with double perforation, bearing two tubes, one of which reaches to the bottom of the flask, whilst the other terminates immediately under the cork. Conduct through the longer tube a slow stream of dry air into the flask, and conduct this, upon its reissuing through the other tube, into a U tube containing a little dilute ammonia, and connected at the other end with an aspirator. The silicofluoric gas which escapes with the air, decomposes with the ammonia, more particularly upon the application of a gentle heat towards the end of the process, fluoride of ammonium and hydrated silicic acid being formed. Filter, evaporate in a platinum crucible to dryness, and examine the residue by 5. For more difficultly decomposable substances bisulphate of potassa is used instead of sulphuric acid, and the mixture, to which some marble is added (to ensure a continuous slight evolution of gas), heated to fusion, and kept in that state for some time.

7. Silicates not decomposable by sulphuric acid must first be fused with four parts of carbonate of soda and potassa. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum vessel, hydrochloric acid added to feebly acid reaction, and the fluid allowed to stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time it is collected on a filter, dried, and examined by the method described in 5 (H. ROSE).

8. Minute quantities of metallic fluorides in minerals, slags, &c., may also be readily detected by means of the *blowpipe*. To this end bend a piece of platinum foil, and insert it in a glass tube as shown in fig. 43, introduce the finely triturated substance mixed with powdered phosphate of soda and ammonia fused on charcoal, and let the blowpipe flame play upon it so that the products of combustion may pass into the tube. A metallic fluoride treated in this way yields hydrofluoric acid gas, which betrays its presence by its pungent odor, the dimming of the glass tube (which becomes perceptible only after cleaning and drying), and the yellow tint which the acid air issuing from the tube imparts to a moist slip of Brazil-wood paper* (BERZELIUS, SMITHSON). When silicates containing metallic fluorides are treated in this manner gaseous fluoride of silicon is formed, which also colors yellow a moist slip of Brazil-wood paper inserted

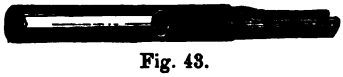

Fig. 43.

* Prepared by moistening slips of fine printing-paper with decoction of Brazil-wood.

in the tube, and leads to silicic acid being deposited within the tube. After washing and drying the tube, it appears here and there dimmed. A small quantity of a fluoride present in a mineral containing water may generally be detected by heating the substance by itself in a glass tube sealed at one end and inserting a slip of Brazil wood paper in the tube; under the circumstance the paper will usually turn yellow (BERZELIUS).

## § 147.

*Recapitulation and remarks.*—The baryta compounds of the acids of the third division are dissolved by hydrochloric acid, apparently without decomposition; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The baryta compounds of the acids of the first division show, however, the same deportment; these acids must, therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a salt of baryta by alkalies. But even leaving this point altogether out of the question no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions the salts of baryta in question, and more particularly the borate of baryta and the fluoride of barium, if the solution contains any considerable proportion of free acid or of an ammoniacal salt. *Boracic acid* is well characterized by the coloration which it imparts to the flame of alcohol, and also by its action on turmeric-paper. The latter reaction is more particularly suited for the detection of very minute traces. Oxides of the heavy metals, if present, are most conveniently removed first by hydrosulphuric acid or sulphide of ammonium. Before proceeding to concentrate dilute solutions of boracic acid the acid must be combined with an alkali, otherwise a large portion of it will volatilize with the aqueous vapors. Small quantities of boracic acid may also be safely and easily detected by the spectroscope. The detection of *phosphoric acid* in compounds soluble in water is not difficult; the reaction with sulphate of magnesia, &c., is the best adapted for the purpose. The detection of phosphoric acid in insoluble compounds cannot be effected by means of magnesia solution. Sesquichloride of iron (§ 142, 9) is well suited for the detection of phosphoric acid in its salts with the alkaline earths, and more particularly for the separation of the acid from the alkaline earths; the nitric acid solution of molybdate of ammonia is more especially adapted to effect the detection of phosphoric acid in presence of alumina and sesquioxide of iron. I must repeat again that both these reactions demand the *strictest* attention to the directions given. If present in combination with oxides of the fourth, fifth, or sixth group, it may be separated by the method given § 142, 11, or by precipitating the bases with hydrosulphuric acid or sulphide of ammonium.

*Oxalic acid* may always be easily detected in aqueous solutions of oxalates of the alkalies, by solution of sulphate of lime. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt the oxalate of lime may be readily distinguished from the racemate, by simple ignition, with exclusion of air, as the decomposed racemate leaves a considerable proportion of

charcoal behind; the racemate dissolves moreover in cold solution of potassa or soda, in which oxalate of lime is insoluble. The deportment of the oxalates with sulphuric acid, or with binoxide of manganese and sulphuric acid, affords also sufficient means to confirm the results of other tests. In insoluble salts the oxalic acid is detected most safely by decomposing them by boiling with solution of carbonate of soda, or by hydrosulphuric acid or sulphide of ammonium (§ 145, 8). I must finally also call attention here to the fact that there are certain soluble oxalates which are not precipitated by salts of lime; these are more particularly oxalate of sesquioxide of chromium, and oxalate of sesquioxide of iron. Their non-precipitation is owing to the circumstance that these salts form soluble double salts with oxalate of lime. *Hydrofluoric acid* is readily detected in salts decomposable by sulphuric acid; only it must be borne in mind that an over large proportion of sulphuric acid impedes the free evolution of hydrofluoric gas, and thus impairs the delicacy of the reaction; also that the glass cannot be distinctly etched if, instead of hydrofluoric gas, fluosilicic gas alone is evolved; and therefore, in the case of compounds abounding in silica, the safer way is to try, besides the reaction given § 146, 5, also the one given in 6. In silicates which are not decomposed by sulphuric acid the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given in 7.

§ 148.

PHOSPHOROUS ACID ($PO_3$).

Anhydrous phosphorous acid is a white powder, which admits of sublimation, and burns when heated in the air. It forms with a small proportion of water a thickish fluid, which crystallizes by long standing. Heat decomposes it into hydrated phosphoric acid, and phosphuretted hydrogen gas, which does not spontaneously take fire. It freely dissolves in water. Of the salts those with alkaline base are readily soluble in water, all the others sparingly soluble; the latter dissolve in dilute acids. All the salts are decomposed by ignition into phosphates, which are left behind, and hydrogen, or a mixture of hydrogen and phosphuretted hydrogen, which escapes. With *nitrate of silver* separation of metallic silver takes place, more especially upon addition of ammonia and application of heat; with *nitrate of suboxide of mercury*, under the same circumstances, separation of metallic mercury. From *chloride of mercury* in excess phosphorous acid throws down subchloride of mercury after some time, more rapidly upon heating. *Chloride of barium* and *chloride of calcium* produce in not over-dilute solutions of phosphorous acid, upon addition of ammonia, white precipitates, soluble in acetic acid. A mixture of sulphate of magnesia, chloride of ammonium, and ammonia will precipitate only rather concentrated solutions. *Acetate of lead* throws down white phosphite of lead, insoluble in acetic acid. By heating to boiling with *sulphurous acid* in excess phosphoric acid is formed, attended by separation of sulphur. In contact with *zinc* and *dilute sulphuric* acid phosphorous acid gives a mixture of hydrogen with phosphuretted hydrogen, which accordingly fumes in the air, burns with an emerald-green color, and precipitates silver and phosphide of silver from solution of nitrate of silver.

*Fourth Division of the First Group of the Inorganic Acids.*

§ 149.

*a.* CARBONIC ACID ($CO_2$).

1. CARBON is a solid tasteless and inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization (DESPRETZ). All carbon is combustible, and yields carbonic acid when

burnt with a sufficient supply of oxygen or atmospheric air. In the diamond the carbon is crystallized, transparent, pellucid, exceedingly hard, difficultly combustible; in the form of graphite it is opaque, blackish-grey, soft, greasy to the touch, difficultly combustible, and stains the fingers; as charcoal produced by the decomposition of organic matter it is black, opaque, non-crystalline—sometimes dense, shining, and difficultly combustible, and sometimes porous, dull, and readily combustible.

2. CARBONIC ACID, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another. It is inodorous, has a sourish taste, and reddens moist litmus-paper; but the red tint disappears again upon drying. Carbonic acid is readily absorbed by solution of potassa; it dissolves pretty copiously in water.

3. The AQUEOUS SOLUTION OF CARBONIC ACID has a feebly acid and pungent taste; it transiently imparts a red tint to litmus-paper, and colors solution of litmus wine-red; it loses its carbonic acid when shaken with air in a half-filled bottle, and more completely still upon application of heat. Some of the CARBONATES lose their carbonic acid by ignition; those with colorless oxides are white or colorless. Of the neutral carbonates only those with alkaline bases are soluble in water. The solutions manifest a very strong alkaline reaction. Besides the carbonates with alkaline bases, those also with an alkaline earth for base, and some of those with a metallic base, dissolve as acid or bicarbonates.

4. The carbonates are decomposed by all free *acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. Most carbonates are decomposed in the cold, but several (magnesite, for instance) require heat. The decomposition is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless and inodorous gas, which transiently imparts a reddish tint to litmus-paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid should first be heated with a little water, to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substances with the acid. Where there is reason to apprehend the escape of carbonic acid upon boiling with water, lime water should be used instead of pure water. If you wish to prove that the escaping gas is really carbonic acid, dip a glass rod in baryta water and hold it inside the test-tube near the fluid; a white pellicle will form on the baryta-water, as is explained in 5.

5. *Lime water* and *baryta-water*, brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME ($CaO, CO_2$), or CARBONATE OF BARYTA ($BaO, CO_2$). In testing for free carbonic acid the reagents ought always to be added in excess, as the acid carbonates of the alkaline earths are soluble in water. The precipitates dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition. As lime-water dissolves very minute quantities of carbonate of lime, the detection of

exceedingly minute traces of carbonic acid requires the use of a lime-water saturated with carbonate of lime by long digestion therewith (WELTER, BERTHOLLET).

6. *Chloride of calcium* and *chloride of barium* immediately produce in solutions of neutral alkaline carbonates, precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTA; in dilute solutions of bicarbonates these precipitates are formed only upon ebullition; with free carbonic acid these reagents give no precipitate.

## § 150.

### *b.* SILICIC ACID ($SiO_2$).

1. SILICIC ACID is colorless or white, even in the hottest blowpipe flame unalterable and infusible. It fuses in the flame of the oxyhydrogen blowpipe. It is met with in the crystalline and the amorphous state. It is insoluble in water and acids (with the exception of hydrofluoric acid, which dissolves the amorphous variety easily, the crystalline variety with more difficulty); its hydrate is soluble in water and acids, but only at the moment of its separation. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of potassa and soda and their carbonates; but the crystallized acid is insoluble or nearly so in these fluids. If either of the two is fused with a caustic alkali or alkaline carbonate, a basic silicate of the alkali is obtained, which is soluble in water. The SILICATES with alkaline bases alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids*. If a large proportion of hydrochloric acid is added at once to even concentrated solutions of alkaline silicates the separated silicic acid remains in solution; but if the hydrochloric acid is added gradually drop by drop, whilst stirring the fluid, the greater part of the silicic acid separates as gelatinous hydrate. The more dilute the fluid, the more silicic acid remains in solution, and in highly dilute solutions no precipitate is formed. If the solution of an alkaline silicate, mixed with hydrochloric or nitric acid in excess, is evaporated to dryness silicic acid separates in proportion as the acid escapes; upon treating the residue with hydrochloric acid and water the silicic acid remains in the free state (or, if the temperature was restricted to 100°, as hydrate), as an insoluble white powder. Chloride of ammonium produces in not over-dilute solutions of alkaline silicates precipitates of hydrate of silicic acid (containing alkali). Heating promotes the separation.

3. Some of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, others are not affected by these acids, even upon boiling. In the decomposition of the former the greater portion of the silicic acid separates usually as gelatinous, more rarely as pulverulent hydrate. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated hydrate of silicic acid suspended in it, is evaporated to dryness, the residue heated with stirring, at a uniform temperature above the boiling point of water until no more acid fumes escape, then moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary insoluble silicic acid. Of the silicates not decomposed by hydrochloric acid many, *e.g.*, kaolin, are completely decomposed by

heating with a mixture of 8 parts of hydrated sulphuric acid and 3 parts of water, the silicic acid being separated in the pulverulent form; many others are acted upon to some extent by this reagent. Silicates not decomposable by boiling with hydrochloric or sulphuric acid in the open air, may generally be completely decomposed by heating in a state of fine powder with the acids in sealed glass tubes at 200°—210° in an air or paraffin bath.

4. If a silicate, reduced to a fine powder, is fused with 4 parts of *carbonate of potassa and soda* until the evolution of carbonic acid has ceased, and the fused mass is then boiled with water, the greater part of the silicic acid dissolves as alkaline silicate, whilst the alkaline earths, the earths proper, (with the exception of alumina and berylla, which pass more or less completely into the solution), and the heavy metallic oxides are left undissolved. If the fused mass is treated with water, then, without previous filtration, hydrochloric or nitric acid added to strongly acid reaction, and the fluid treated as directed in 3, the silicic acid is left undissolved, whilst the bases are dissolved. If the powdered silicate is fused with 4 parts of hydrate of baryta, the fused mass digested with water, with addition of hydrochloric or nitric acid, and the acid solution treated as directed in 3, the silicic acid separates, and the bases, especially also the alkalies, are found in the filtrate.

5. If *hydrofluoric acid*, in concentrated aqueous solution or in the gaseous state, is made to act upon silicic acid, fluosilicic gas escapes ($Si O_2 + 2 H F = Si F_2 + 2 H O$); dilute acid dissolves silica to hydrofluosilicic acid ($Si O_2 + 3 H F = Si F_2, H F + 2 H O$). Hydrofluoric acid acting upon silicates gives rise to the formation of silicofluorides ($Ca O, Si O_2 + 3 H F = Si F_2, Ca F + 3 H O$), which by heating with hydrated sulphuric acid are changed to sulphates, with evolution of hydrofluoric and fluosilicic gas. If the powdered silicate is mixed with 3 parts of fluoride of ammonium, or 5 parts of fluoride of calcium in powder, the mixture made into a paste with hydrated sulphuric acid, and heat applied (best in the open air) until no more fumes escape, the whole of the silicic acid present volatilizes as fluosilicic gas. The bases present are found in the residue as sulphates, mixed, if fluoride of calcium was used, with sulphate of lime.

6. On mixing 1 part of finely powdered silica, or a silicate with 2 parts of powdered cryolite or fluor spar (free from silica), and 4 or 5 parts of concentrated sulphuric acid, heating the mixture moderately in a platinum crucible, but not allowing it to spurt, and then holding close over the surface the loop of a stout platinum wire which has been freshly ignited, and now contains a drop of water; a pellicle of hydrated silicic acid will soon form on the latter from decomposition of the escaping fluosilicic gas (BARFOED).

7. If silicic acid or a silicate is fused with *carbonate of soda* in the loop of a platinum wire FROTHING is observed in the bead owing to the evolution of carbonic acid. The bead obtained with pure silicic acid is always clear when hot, with silicates when they are rich in silicic acid (as the felspathic rocks), the bead is also clear, otherwise it is opaque. The clearness of the cold bead depends upon the proportion between silicic acid, soda, and other bases.

8. *Phosphate of soda and ammonia*, in a state of fusion, fails nearly altogether to dissolve silicic acid. If therefore silicic acid or a silicate is fused, in small fragments, with phosphate of soda and ammonia on a

platinum wire the bases are dissolved, whilst the silicic acid separates and floats about in the clear bead as a more or less translucent mass, exhibiting the shape of the fragment of substance used.

## § 151.

*Recapitulation and remarks.*—Free carbonic acid is readily known by its reaction with lime-water; the carbonates are easily detected by the evolution of an inodorous gas, when they are treated with acids. When operating upon compounds which evolve other gases besides carbonic acid, the gas is to be tested with lime-water or baryta-water. Silicic acid, both in the free state and in silicates, may usually be readily detected by the reaction with phosphate of soda and ammonia. It differs moreover from all other bodies in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and in fusing bisulphate of potassa, and its solubility in boiling solutions of alkalies and alkaline carbonates; and from many bodies (especially from titanic acid) by completely volatilizing upon repeated evaporation in a platinum dish, with hydrofluoric acid (or fluoride of ammonium) and sulphuric acid.

### *Second Group.*

ACIDS WHICH ARE PRECIPITATED BY NITRATE OF SILVER, BUT NOT BY CHLORIDE OF BARIUM: *Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrocyanic Acid, Hydroferro-* and *Hydroferricyanic Acid, Hydrosulphuric Acid* (Nitrous Acid, Hypochlorous Acid, Chlorous Acid, Hypophosphorous Acid).

The silver compounds corresponding to the *hydrogen acids* are insoluble in dilute nitric acid. These acids decompose with metallic oxides, the metals combining with the chlorine, bromine, iodine, cyanogen, or sulphur, whilst the oxygen of the metallic oxide forms water with the hydrogen of the acid.

## § 152.

### *a.* HYDROCHLORIC ACID (H Cl).

1. CHLORINE is a heavy yellowish-green gas of a disagreeable and suffocating odor, which has a most injurious action upon the respiratory organs; it destroys vegetable colors (litmus, indigo-blue, &c.); it is not inflammable, and supports the combustion of few bodies only. Minutely-divided antimony, tin, &c., spontaneously ignite in it, and are converted into chlorides. It dissolves pretty freely in water; the chlorine water formed has a faint yellowish-green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 29), and loses its smell when shaken with mercury, the latter being converted into a mixture of subchloride and metal. Small quantities of free chlorine may be readily detected in a fluid by the red color imparted to a mixture of sulphocyanide of potassium and protosalt of iron, or—in the absence of nitrous acid—by the blue color imparted to a mixture of starch paste and iodide of potassium (see § 154, 9).

2. HYDROCHLORIC ACID, at the common temperature and common atmospheric pressure, is a colorless gas, which forms dense fumes in the air, is suffocating and very irritant, and dissolves in water with exceeding facility. The concentrated solution (fuming hydrochloric acid) loses a large portion of its gas upon heating.

3. The neutral METALLIC CHLORIDES are readily soluble in water, with the exception of chloride of lead, chloride of silver, and subchloride of mercury; most of the chlorides are white or colorless. Many of them volatilize at a high temperature, without suffering decomposition; others are decomposed upon ignition, and many of them are fixed at a moderate red heat.

4. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides white precipitates of CHLORIDE OF SILVER (Ag Cl), which upon exposure to light change first to violet, then to black; they are insoluble in dilute nitric acid, but dissolve readily in ammonia as well as in cyanide of potassium, and fuse without decomposition when heated. (Compare § 115, 7.)

5. *Nitrate of suboxide of mercury and acetate of lead* produce in solutions containing free hydrochloric acid or metallic chlorides precipitates of SUBCHLORIDE OF MERCURY ($Hg_2Cl$) and CHLORIDE OF LEAD (Pb Cl). For the properties of these precipitates see § 116, 6, and § 117, 7.

6. If hydrochloric acid is heated with *binoxide of manganese*, or a chloride with *binoxide of manganese* and *sulphuric acid*, CHLORINE is evolved, which may be readily recognised by its odor, its yellowish-green color, and its bleaching action upon vegetable colors. The best way of testing the latter is to expose to the gas a moist slip of litmus-paper, or of paper coloured with solution of indigo.

7. If a metallic chloride is triturated with *chromate of potassa*, the dry mixture treated with *concentrated sulphuric acid* in a tubulated retort, and a gentle heat applied, a deep brownish-red gas is copiously evolved (CHLOROCHROMIC ACID, $CrO_2Cl$), which condenses into a fluid of the same color, and passes into the receiver. If this distillate is mixed with ammonia in excess, a yellow-colored liquid is produced, from the formation of chromate of ammonia ($CrO_2Cl + 2NH_4O = NH_4Cl + NH_4O, CrO_3$). Upon addition of an acid the color of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

8. In the metallic chlorides insoluble in water and nitric acid the chlorine is detected by fusing them with carbonate of soda and potassa, and treating the fused mass with water, which will dissolve, besides the excess of the alkaline carbonate, the chloride of the alkali metal formed in the process.

9. If in a bead of *phosphate of soda and ammonia* on a platinum wire *oxide of copper* be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it so long as chlorine is present (BERZELIUS.) With respect to the spectrum of chloride of copper, compare § 157.

## § 153.

### *b.* HYDROBROMIC ACID (H Br).

1. BROMINE is a heavy reddish-brown fluid of a very disagreeable chlorine-like odor; it boils at 63°, and volatilizes rapidly even at the common temperature. The vapor is brownish-red. Bromine bleaches vegetable colors like chlorine; it is pretty soluble in water, but dissolves more readily in alcohol, and very freely in ether. The solutions are yellowish-red.

2. HYDROBROMIC ACID GAS, its AQUEOUS SOLUTION, and the METALLIC BROMIDES offer in their general deportment a great analogy to the corresponding chlorides.

3. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid or of bromides a yellowish-white precipitate of BROMIDE OF SILVER (Ag Br), which changes to gray upon exposure to light; this precipitate is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia, but dissolves with facility in cyanide of potassium.

4. *Nitrate of protoxide of palladium*, but not protochloride of palladium, produces in neutral solutions of metallic bromides a reddish-brown precipitate of PROTOBROMIDE OF PALLADIUM. In concentrated solutions this precipitate is formed immediately; in dilute solutions it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury, upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. In the case of a solution, the liberated bromine colors it yellow or yellowish-red. With bromides in the solid state or in concentrated solution, brownish-red (if diluted, brownish-yellow) vapors of bromine gas escape at the same time, which, if evolved in sufficient quantity, condense in the cold part of the test-tube to small drops. In the cold, nitric acid, even the red fuming, fails to liberate the bromine in very dilute solutions of bromides, nor is it liberated by solution of hyponitric acid in hydrated sulphuric acid, or by hydrochloric acid and nitrite of potassa.

6. *Chlorine*, in the *gaseous* state or in *solution*, immediately liberates bromine in the solutions of its compounds; the fluid assuming a yellowish-red tint if the quantity of the bromine present is not too minute. A large excess of chlorine must be avoided, since this will cause formation of chloride of bromine, which will destroy the color wholly or nearly so. This reaction is made much more delicate by addition of a fluid which dissolves bromine and does not mix with water, as sulphide of carbon or chloroform. Mix the neutral or feebly acid solution in a test-tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine-water drop by drop, and shake the tube. With appreciable quantities of bromine, *e.g.* 1 part in 1000 parts of water, the drop at the bottom acquires a reddish-yellow tint; with very minute quantities (1 part of bromine in 30,000 parts of water), a pale yellow tint, which, however, is still distinctly discernible. Ether was formerly used for this reaction; this agent is *by no means* so well suited for it. A large excess of chlorine-water must be avoided in this experiment also, and it must always be ascertained first whether the chlorine-water, mixed with a large quantity of water and some

sulphide of carbon or chloroform, and shaken, will leave these reagents quite uncolored. If not, the chlorine-water is not suited for the intended purpose. If the solution of bromine in sulphide of carbon or chloroform (or ether) is mixed with some solution of potassa, the mixture shaken, and heat applied, the yellow color disappears, and the solution now contains bromide of potassium and bromate of potassa. By evaporation and ignition the bromate of potassa is converted into bromide of potassium, and the ignited mass may then be further tested as directed in 7.

7. If bromides are heated with *binoxide of manganese* and *hydrated sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. Presence of chlorides in large proportion is not favourable to the reaction and requires addition of some water, and the sulphuric acid to be added gradually in *very small* quantities. If the bromine is present only in very minute quantity, the color of these vapors is not visible. But if the mixture is heated in a small retort, and the evolved vapors are transmitted through a long glass condenser, the color of the bromine vapors may generally be seen by looking lengthways through the tube, and the first drops of the distillate are also colored yellow. The first vapors and the first drops of the distillate should be received in a test-tube containing some starch moistened with water; since

8. If moistened *starch* is brought into contact with free bromine, more especially in form of vapor, YELLOW BROMIDE OF STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by sealing the test-tube which contains the moistened starch and the first drops of the distillate from 7, and then cautiously inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time, will again disappear. The reaction may be called forth in a simple manner, almost with the same degree of delicacy, by gently heating the fluid containing free bromine, or also the original mixture of bromide, binoxide of manganese, and sulphuric acid, in a very small beaker, covered with a watch-glass with a slip of paper attached to the lower side, moistened with starch paste, and sprinkled with starch powder.

9. If sulphuric acid is poured over a mixture of a bromide with *chromate of potassa*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over does not turn yellow, but becomes colorless upon supersaturation with ammonia.

10. If a solution of hydrobromic acid or a bromide is mixed with a little *chloride of gold* a straw color or dark orange color is produced from the formation of BROMIDE OF GOLD. If iodine is present it must be removed before the solution of gold is added (BILL).

11. In the metallic bromides which are insoluble in water and nitric acid, the bromine is detected in the same way as the chlorine in the corresponding chlorides.

12. If a substance containing bromine is added to a *phosphate of soda and ammonia bead saturated with oxide of copper*, and the bead is then ignited in the inner blowpipe flame, the flame is colored BLUE, inclining to GREEN, more particularly at the edges (BERZELIUS). With regard to the spectrum of bromide of copper see § 157.

## § 154.

### *e.* Hydriodic Acid (H I).

1. Iodine is a solid soft body of a peculiarly disagreeable odor. It is generally seen in the form of black, shining, crystalline scales. It fuses at a gentle heat; at a somewhat higher temperature it is converted into vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol and ether, as well as in solution of iodide of potassium. The aqueous solution is light-brown, the alcoholic, ethereal, and iodide of potassium solutions are deep red-brown. Iodine destroys vegetable colors only slowly and imperfectly; it stains the skin brown; with starch it forms a compound of an intensely deep blue color. This compound is formed invariably where iodine vapor or a solution containing free iodine comes in contact with starch, best with starch-paste. It is decomposed by alkalies, by chlorine and bromine, and by sulphurous acid and other reducing agents.

2. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas; it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown in contact with the air, water being formed, and a solution of iodine in hydriodic acid.

3. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colors, *e.g.* iodide of lead, subiodide and iodide of mercury.

4. *Nitrate of silver* produces in aqueous solutions of hydriodic acid and of iodides yellowish-white precipitates of iodide of silver (Ag I), which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and *very sparingly soluble in ammonia*, but dissolve readily in cyanide of potassium.

5. *Protochloride of palladium* and *nitrate of protoxide of palladium* produce even in very dilute solutions of hydriodic acid or metallic iodides, a brownish-black precipitate of protiodide of palladium, which dissolves to a trifling extent in saline solutions (chloride of sodium, chloride of magnesium, &c.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

6. A solution of 1 part of *sulphate of copper* and $2\frac{1}{2}$ parts of *sulphate of protoxide of iron* throws down from neutral aqueous solutions of the iodides subiodide of copper ($Cu_2I$), in the form of a dirty white precipitate. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent. Instead of using the mixture of sulphates, sulphate of copper alone may be added, and afterwards enough sulphurous acid to remove the brown colour produced by separated iodine.

7. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic acid or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *hyponitric acid* decompose hydriodic acid and iodides with the greatest facility even in the most dilute solutions. Colorless solutions of iodides therefore acquire immediately a brownish-red color upon addition of some red fuming nitric acid, or of a mixture of this with concentrated

sulphuric acid, or, better still, upon addition of a solution of hyponitric acid in hydrated sulphuric acid, or of nitrite of potassa and some sulphuric or hydrochloric acid. From more concentrated solutions the iodine separates in the form of black scales, whilst nitric oxide and iodine vapor escape.

8. As the blue coloration of iodide of starch remains visible in much more highly dilute solutions than the yellow color of solution of iodine in water, the delicacy of the reaction just now described (7) is considerably heightened by mixing the fluid to be tested for iodine first with some thin tolerably clear *starch-paste*, then adding a few drops of dilute sulphuric acid, to make the fluid strongly acid, and finally one of the reagents given in 7. Of the solution of hyponitric acid in sulphuric acid a single drop on a glass rod suffices to produce the reaction most distinctly. I can therefore strongly recommend this reagent, which was first proposed by OTTO. Red fuming nitric acid must be added in somewhat larger quantity, to call forth the reaction in its highest intensity; this reagent therefore is not well adapted to detect very minute quantities of iodine. The reaction with nitrite of potassa also is very delicate. The fluid to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of nitrite of potassa is then added. In cases where the quantity of iodine present is very minute the fluid turns reddish, instead of blue. An excess of the fluid containing nitrous acid or hyponitric acid does not materially impair the delicacy of the reaction. As iodide of starch dissolves in hot water to a colorless liquid, the fluids must of necessity be cold; the colder they are the more delicate the reaction. To attain the highest degree of delicacy, cool the fluid with ice, let the starch deposit, and place the test-tube upon white paper to observe the reaction (compare also § 157).

9. *Chlorine gas* and *chlorine-water* decompose compounds of iodine also, setting the iodine free; but if the chlorine is applied in excess the liberated iodine combines with it to colorless chloride of iodine. A dilute solution of the metallic iodide, mixed with starch-paste, acquires therefore upon addition of a little chlorine-water at once a blue tint, but becomes colorless again upon addition of more chlorine-water. As it is therefore difficult not to exceed the proper limit, especially where the quantity of iodine present is only small, chlorine-water is not well-adapted for the detection of minute quantities of iodine.

10. If a solution containing hydriodic acid or an iodide is mixed with *chloroform* or *sulphide of carbon*, so as to leave a few drops undissolved, and one of the agents by which iodine is liberated (a drop of a solution of hyponitric acid in sulphuric acid—hydrochloric acid and nitrite of potassa—chlorine-water, &c.) is added, the mixture vigorously shaken, and then allowed to stand at rest, the chloroform or the sulphide of carbon, colored a deeper or lighter violet-red by the iodine dissolved in it, subsides to the bottom. This reaction also is exceedingly delicate. If a solution containing free iodine is shaken with *petroleum*, *benzol*, or *ether*, the two former are colored red, the ether reddish-brown or yellow. Iodine colors ether much more intensely than an equal quantity of bromine.

11. If metallic iodides are heated with *concentrated sulphuric acid*, or with *sulphuric acid* and *binoxide of manganese*, or with *sulphuric acid*

and *chromate of potassa*, or with *sesquichloride of iron* and a little *hydrochloric acid*, iodine separates, which may be known by the color of its vapor, or in the case of very minute quantities, by its action upon a slip of paper coated with starch-paste.

12. The iodides which are insoluble in water and nitric acid comport themselves upon fusion with *carbonate of soda and potassa* in the same manner as the corresponding chlorides.

13. A *phosphate of soda and ammonia bead saturated with oxide of copper*, when touched with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN color to the flame. With regard to the spectrum of iodide of copper see § 157.

## § 155.

### *d.* HYDROCYANIC ACID (H Cy).

1. CYANOGEN is a colorless gas of a peculiar penetrating odor; it burns with a crimson flame, and is pretty soluble in water.

2. HYDROCYANIC ACID is a colorless, volatile, inflammable liquid, the odor of which distantly resembles that of bitter almonds; it is miscible with water in all proportions; in the pure state it speedily suffers decomposition. It is extremely poisonous.

3. The CYANIDES with alkalies and alkaline earths are soluble in water; the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid. Cyanides of potassium and sodium are not decomposed by fusion if air is excluded; when fused with oxides of lead, copper, antimony, tin, &c., they reduce these oxides, and are converted into cyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed by ignition, the cyanides of the noble metals being converted into cyanogen gas and metal, the cyanides of the other heavy metals into nitrogen gas and metallic carbides. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. By heating and evaporation with concentrated sulphuric acid all cyanides are decomposed; hydrochloric acid decomposes a few of them; hydrosulphuric acid decomposes many cyanides.

4. The CYANIDES have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in cyanide of potassium. The resulting compounds are either:

*a.* True double salts, compounds of the second order, *e.g.*, K Cy + Ni Cy. From solutions of such double salts acids, by decomposing the cyanide of potassium, precipitate the metallic cyanide which was combined with it.—Or,

*b.* Simple haloid salts, compounds of the first order, in which a metal *e.g.*, potassium, is combined with a compound radical consisting of cyanogen and another metal (iron, cobalt, manganese, chromium). The ferro- and the ferricyanide of potassium, ($K_2Cy_3Fe$ or $K_3Cfy$ and $K_3Cy_6Fe_2$ or $K_3Cfdy$,) and cobalticyanide of potassium, ($K_3Cy_6Co_2$), are compounds of this kind. From solutions of compounds of this nature dilute acids do not separate metallic cyanides in the cold. If the potassium is replaced by hydrogen, peculiar hydrogen acids are formed, which must not be confounded with hydrocyanic acid.

We will now first consider the reactions of hydrocyanic acid and the simple cyanides, then, in an appendix to this paragraph, those of hydroferro- and hydroferricyanic acid.

5. *Nitrate of silver* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals white precipitates of CYANIDE OF SILVER (Ag Cy), which are readily soluble in cyanide of potassium, dissolve with some difficulty in ammonia, and are insoluble in dilute nitric acid; these precipitates are decomposed by ignition, leaving metallic silver with some paracyanide of silver.

6. If a solution of *sulphate of protoxide of iron* and a few drops of *sesquichloride of iron* are added to a solution of free hydrocyanic acid no alteration takes place; but if *solution of potassa* or *soda* is now added a bluish-green precipitate forms, which consists of a mixture of Prussian-blue ($Fe_4 Cfy_3$), and hydrate of protosesquioxide of iron. Upon now adding hydrochloric acid (best after previous application of heat) the hydrate of protosesquioxide of iron dissolves, whilst the PRUSSIAN-BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same final reaction is observed when a mixture of protosalt and persalt of iron is mixed with the solution of an alkaline cyanide, and hydrochloric acid is then added.

7. If a liquid containing a little hydrocyanic acid or cyanide of potassium is mixed with sufficient yellow sulphide of ammonium to impart a yellowish tint to the fluid, then with a little ammonia, and the mixture is warmed in a porcelain dish, with renewal of the water if necessary, until it has become colorless, and the excess of sulphide of ammonium is decomposed or volatilized, the fluid contains now sulphocyanide of ammonium, and after being acidified with hydrochloric acid (which must not be attended with disengagement of hydrosulphuric gas), acquires a blood-red tint upon addition of sesquichloride of iron (v. LIEBIG). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into sulphocyanide of ammonium: $N H_4 S_6 + 2 (N H_4 O) + 2 H Cy = 2 (N H_4 Cy S_2) + N H_4 S + 2 H O$. If an acetate is present the reaction takes place only upon addition of more hydrochloric acid. To discover the cyanogen *in insoluble compounds* by converting it into sulphocyanide of iron you may proceed as follows:—Fuse some hyposulphite of soda in the loop of a platinum wire till the water of crystallization has escaped, and the mass swells out, dip it in the substance, heat for a little time, removing it from the flame as soon as the sulphur begins to burn, and then dip the mass in a few drops of ferric chloride mixed with a little hydrochloric acid. A permanent blood-red color will be produced. If the substance is heated too long the reaction fails, as the sulphocyanide of sodium formed is then destroyed again. This method is well suited to distinguish chloride, bromide, or iodide of silver from cyanide of silver (A. FRÖHDE).

8. On mixing a moderately concentrated solution of an alkaline cyanide with a little picric acid solution (1 of picric acid to 250 of water) and boiling, the fluid appears dark-red from formation of picrocyanate of potassa, the coloration increasing in intensity by standing. If the solution of the alkaline cyanide is very dilute, no more

picric acid must be added than is sufficient just to color the fluid lemon-yellow. After boiling, the red coloration often does not make its appearance till the fluid has cooled and stood some time. The reaction is very delicate (C. D. BRAUN).

9. On saturating filter paper with freshly prepared tincture of guaiacum containing 3 or 4 per cent. of the resin, allowing the alcohol to evaporate, moistening the paper with solution of sulphate of copper containing $\frac{1}{4}$ per cent. of the salt, and then exposing it to air, in which a trace of hydrocyanic acid is present, it becomes blue from a separation of active oxygen. $3\,CuO + 2\,HCy = Cu_2Cy, CuCy + 2\,HO + O$ (PAGENSTECHER, SCHÖNBEIN).

10. If a very dilute solution of iodide of starch is mixed with a trace of hydrocyanic acid, or after addition of dilute sulphuric acid, with a trace of an alkaline cyanide, the blue color will disappear immediately, or after a short time, the iodine and the hydrocyanic acid being transformed into iodide of cyanogen and hydriodic acid (SCHÖNBEIN). This is a very delicate reaction, but cannot be relied upon without further tests, as many other substances decolorize iodide of starch.

11. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound the solution is mixed with hydrosulphuric acid: sulphide of mercury precipitates, and the solution contains free hydrocyanic acid. In solid cyanide of mercury the cyanogen is most readily detected by heating in a glass tube. (Compare 3.)

*Appendix.*

*a. Hydroferrocyanic acid* ($H_2Cfy$). Hydroferrocyanic acid is soluble in water. Some of the ferrocyanides, as those containing metals of the alkalies and alkaline earths, are soluble in water; but the greater part of them are insoluble in that menstruum. All the ferrocyanides are decomposed by ignition; where they are not quite anhydrous, hydrocyanic acid, carbonic acid, and ammonia escape, otherwise nitrogen and occasionally cyanogen. In solutions of hydroferrocyanic acid or of soluble ferrocyanides *sesquichloride of iron* produces a blue precipitate of FERROCYANIDE OF IRON ($Fe_4Cfy_3$); *sulphate of copper* a brownish-red precipitate of FERROCYANIDE OF COPPER ($Cu_2Cfy$); *nitrate of silver* a white precipitate of FERROCYANIDE OF SILVER ($Ag_2Cfy$), which is insoluble in nitric acid and in ammonia, but dissolves in cyanide of potassium. If a not too dilute solution of an alkaline ferrocyanide is mixed with *hydrochloric acid*, and some *ether* is poured on the top of the mixture, HYDROFERROCYANIC ACID will separate in the crystalline form where the two fluids meet. Insoluble ferrocyanides are decomposed by boiling with solution of soda, ferrocyanide of sodium being formed, and the oxides thrown down, unless they are soluble in soda. If ferrocyanides are heated with a mixture of 3 parts concentrated sulphuric acid, and 1 part water, till the free acid is expelled, they are decomposed, and the cyanogen is driven off in the form of hydrocyanic acid; the metals remain behind as sulphates. On projecting metallic cyanides into fusing nitrate of potassa, the cyanogen is converted into carbonic acid and nitrogen, and the metals are converted into oxides, which remain in the crucible

*b. Hydroferricyanic acid* ($H_3$Cfdy). Hydroferricyanic acid and many of the ferricyanides are soluble in water; all ferricyanides are decomposed by ignition like the ferrocyanides. In the aqueous solutions of hydroferricyanic acid and its salts *sesquichloride of iron* produces no blue precipitate; but *sulphate of protoxide of iron* produces a blue precipitate of PROTOFERRICYANIDE OF IRON (3 Fe, Cfdy); *sulphate of copper* a yellowish green precipitate of FERRICYANIDE OF COPPER (3 Cu, Cfdy), which is insoluble in hydrochloric acid; *nitrate of silver* an orange-colored precipitate of FERRICYANIDE OF SILVER (3 Ag, Cfdy), which is insoluble in nitric acid, but dissolves readily in ammonia and in cyanide of potassium. The insoluble ferricyanides are decomposed by boiling with solution of soda, the metallic oxides being thrown down; in the fluid filtered off from them either ferricyanide of sodium alone is found, or a mixture of ferro- with ferricyanide of sodium. By heating with a mixture of 3 parts concentrated sulphuric acid, and 1 part water, and also by fusing with nitrate of potassa, the ferricyanides are decomposed like the ferrocyanides.

## § 156.

### *e.* HYDROSULPHURIC ACID (HS).

1. SULPHUR is a solid, brittle, friable, tasteless body, insoluble in water. It occurs occasionally in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish color, and occasionally in that of a yellow or yellowish-white, or grayish-white powder. It melts at a moderate heat; upon the application of a stronger heat it is converted into brownish yellow vapors, which in cold air condense to a yellow powder, and on the sides of the vessel to drops. Heated in the air it burns with bluish flame to sulphurous acid, which betrays its presence at once by its suffocating odor. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of chlorate of potassa and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid; in boiling solution of soda sulphur dissolves to a yellow fluid, which contains sulphide of sodium and hyposulphite of soda; in cold ammonia it is insoluble, in warm ammonia it dissolves to a small extent. Sulphide of carbon dissolves the ordinary variety of sulphur with ease, but there is a kind which is insoluble in this menstruum.

2. HYDROSULPHURIC ACID, at the common temperature, and under common atmospheric pressure, is a colorless inflammable gas, soluble in water, readily recognised by its smell of rotten eggs; it transiently imparts a red tint to litmus-paper.

3. Of the SULPHIDES only those with alkalies and alkaline earths are soluble in water. These, as well as the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of hydrosulphuric acid gas, which may be readily detected by its smell, and by its action upon solution of lead (see 4). The decomposition of higher sulphides is attended also with separation of sulphur in a finely-divided state; the white precipitate may be readily distinguished from similar precipitates by its deportment on heating. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrosulphuric acid gas,

whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury, gold, and platinum, resist the action of both acids, but dissolve in nitrohydrochloric acid. Upon the solution of sulphides in nitric acid, and in nitrohydrochloric acid, sulphuric acid is formed, and in most cases sulphur is also separated. Many metallic sulphides, more especially those of a higher degree of sulphuration, give a sublimate of sulphur when heated in a tube sealed at one end. All sulphides are decomposed by fusion with nitrate of potassa and carbonate of soda; on extracting the fusion with water the sulphur is found in solution as alkaline sulphate.

4. If hydrosulphuric acid, in the gaseous state or in solution, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of SULPHIDE OF SILVER or SULPHIDE OF LEAD are formed. In cases therefore where the odor fails to afford sufficient proof of the presence of hydrosulphuric acid, these reagents will remove all doubt. If the hydrosulphuric acid is present in the gaseous form the air suspected to contain it is tested by placing in it a small slip of paper moistened with solution of acetate of lead and a little ammonia; if the gas is present the slip becomes covered with a brownish-black shining film of sulphide of lead. To detect a trace of an alkaline sulphide in presence of a free alkali or an alkaline carbonate, the best way is to mix the fluid with a solution of oxide of lead in soda, which is prepared by mixing solution of acetate of lead with solution of soda until the precipitate which forms at first is redissolved.

5. If a fluid containing hydrosulphuric acid or an alkaline sulphide is mixed with solution of soda, then with *nitroprusside of sodium*,* it acquires a fine reddish-violet tint. The reaction is very delicate; but that with solution of oxide of lead in soda is still more sensitive.

6. If metallic sulphides are exposed to the *oxidizing flame of the blowpipe*, the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphurous acid. If a metallic sulphide is heated in a glass tube open at both ends, in the upper part of which a slip of blue litmus-paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphurous acid reddens the litmus-paper.

7. If a finely-pulverized metallic sulphide is boiled in a porcelain dish with solution of potassa, and the mixture heated to incipient fusion of the hydrate of potassa, or if the test specimen is fused in a platinum spoon with hydrate of potassa, and the mass is, in either case, dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the fluid warmed, a brownish-black film of sulphide of silver forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime (v. KOBELL).

8. If the powder of a sulphide which hydrochloric acid will not, or only with difficulty, decompose is mixed in a small cylinder, or in a wide-necked flask, with an equal volume of finely-divided iron free from sulphur (ferrum alcoholisatum), and some moderately dilute hydrochloric acid (1 volume of concentrated acid to 1 volume of water) is poured over the mixture, in a layer a few lines thick, hydrosulphuric acid escapes along with the hydrogen. This may be easily detected by placing a slip of

* Nitroprusside of sodium being a reagent which can very well be dispensed with, I have omitted giving it a place among the reagents.

paper moistened with solution of acetate of lead, and dried again, under the cork, so that the bottom is covered by it, the ends of the slip projecting on both sides, and then loosely inserting the cork into the mouth of the flask. Realgar, orpiment, and molybdenite do not show this reaction (v. KOBELL).

## § 157.

*Recapitulation and remarks.*—Most of the acids of the first group are also precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are soluble in dilute nitric acid, whilst the latter are insoluble in that menstruum. The presence of hydrosulphuric acid interferes more or less with the testing for the other acids of the second group; this acid must therefore, if present, be removed first before the testing for the other acids can be proceeded with. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition; and when present in the form of an alkaline sulphide, by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. Hydriodic and hydrocyanic acids may be detected, even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch or sulphide or carbon (with addition of a fluid containing nitrous acid), and with solution of protosesquioxide of iron. But the detection of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. These latter must therefore, if present, be removed first before the proper tests for chlorine and bromine can be applied. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into salts of silver, and igniting: the cyanide of silver is decomposed in this process, whilst the chloride, bromide, and iodide of silver remain unaltered. Upon fusing the ignited residue with carbonate of soda and potassa, and boiling the fused mass with water, chloride, bromide, and iodide of the alkali metals are obtained in solution. The fused silver compounds may also be readily decomposed with zinc; all that is required for this purpose is to pour water over them, to add a little sulphuric acid and a fragment of zinc, to let the mixture stand some time, and finally to filter the solution of chloride, bromide, or iodide of zinc from the separated metallic silver.

The iodine may be separated from the chlorine and bromine, by treating the silver compounds with ammonia, but more accurately by precipitating the iodine as subiodide of copper. From bromine iodine is separated most accurately by protochloride of palladium, which only precipitates the iodine; from chlorine it is separated by nitrate of protoxide of palladium.

Bromine in presence of iodine and chlorine may be identified by the following simple operation: Mix the fluid with a few drops of dilute sulphuric acid, then with some starch-paste, and add a little red fuming nitric acid or, better still, a solution of hyponitric acid in sulphuric acid, whereupon the iodine reaction will show itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared; then add some more chlorine-water to set the bromine also free, which may then be separated and identified by means of chloroform or sulphide of

carbon. Or the iodine after being liberated in a highly dilute fluid may be also taken up with chloroform or sulphide of carbon, the aqueous fluid may then be filtered through a moist filter, and the bromine detected in the filtrate by means of chloroform or sulphide of carbon and chlorine-water. For the latter process you may substitute the following: immediately after the liberation of the iodine cautiously add chlorine-water, when the violet-red coloration will gradually fade away, and give place to the brownish-red color indicative of bromine.

The detection of chlorides in presence of bromides and iodides is best effected by precipitating with nitrate of silver, washing the precipitate, digesting it with a mixture of 1 part ammonia and 3 parts water, filtering off the iodide of silver, precipitating the filtrate with nitric acid, washing the precipitate (which contains chloride and bromide of silver with a trace of iodide), drying it, fusing with carbonate of soda, extracting the fusion with water, neutralizing the solution with sulphuric acid (the reaction may be somewhat alkaline), evaporating to dryness, fusing the residue with bichromate of potassa, and treating the fusion according to § 152, 7. The presence of much iodine interferes with the reaction, therefore it is directed to be removed.

As regards the iodide of starch reaction, it must be noted that salts (alum, alkaline sulphates, sulphate of magnesia, &c.) diminish its delicacy. Also as regards this and the sulphide of carbon reaction, that when hyponitric acid is used to liberate the iodine, the presence of sulphocyanides may occasion mistakes (NADLER), since a reddish color may occur in the absence of iodine from formation of pseudosulphocyanogen. By shaking with sulphide of carbon the coloring substance is for the most part taken up.

Besides the above mentioned agents for liberating iodine many others have been proposed, and may be employed; thus, for instance, iodic acid or alkaline iodate and hydrochloric acid (v. LIEBIG); sesquichloride of iron and sulphuric acid, or bichloride of platinum, with addition of some hydrochloric acid (HEMPEL); permanganate of potassa in slightly acidified solution (HENRY), &c. With respect to these agents I have to observe that iodic acid must be used with the greatest caution, as *a*, in presence of reducing substances iodine is set free from the reagent, and *b*, an excess of iodic acid will at once put an end to the reaction. Sesquichloride of iron, with addition of sulphuric acid, will not act immediately upon very dilute solutions; but after a time the reaction will make its appearance, revealing the presence of even the minutest trace of iodine; the delicacy of the reaction is not materially impaired by an excess of the reagent. Sesquichloride of iron may be used with advantage when iodine is to be liberated in the gaseous state, which should be done in the presence of sulphocyanides. The fluid is then heated nearly to boiling, and the escaping fumes are made to act on paper smeared with fresh starch paste. Permanganate of potassa acts immediately, even in the most dilute solutions. However, as a fluid colored by minute traces of iodide of starch is also apt to look reddish, the coloration imparted by the permanganic acid alone may lead to mistakes in the iodide of starch test. From six to twelve hours should therefore always be allowed to elapse before judging of the actual nature of the coloration. The *modus operandi* may of course be modified in various ways to increase the delicacy of the starch reaction; interesting

particulars upon this point may be found in the papers of MORIN* and HEMPEL.†

Chlorine, bromine, and iodine, may also be distinguished from each other by the spectroscope, for the spectra of their copper salts, though containing many blue and green lines, vary in the position and prominence of the lines; they may also be detected in presence of one another, for by cautiously heating the silver salts with oxide of copper in a current of hydrogen, and lighting the escaping gas, the flame will be colored first by the chloride of copper, then by the bromide of copper, and lastly by the iodide of copper (AL. MITSCHERLICH).‡ The use of this method requires considerable practice in consequence of the similarity of the spectra, and the method therefore appears to me of more scientific interest than practical importance.

## § 158.

### *Rarer Acids of the Second Group.*

### 1. NITROUS ACID ($NO_3$).

Nitrous acid, in the free state, at the common temperature, is a brownish-red gas. In contact with water it is converted for the most part, at least, into nitric acid, which dissolves, and nitric oxide, which escapes in part when the quantity of water is not very large ($3NO_3+HO=HO,NO_5+2NO_2$). The nitrites are decomposed by ignition; many of them are soluble in water. When nitrites or concentrated solutions of nitrites are treated with dilute sulphuric acid it is not nitrous acid gas which is evolved, but nitric oxide gas, and the evolution is attended with formation of nitric acid. In solutions of nitrites of the alkalies *nitrate of silver* produces a white precipitate, which dissolves in a very large proportion of water, especially upon application of heat; *sulphate of protoxide of iron*, upon addition of a small quantity of acid, produces a dark blackish-brown coloration, which is due to the nitric oxide gas dissolving in the solution of the sulphate of iron. *Hydrosulphuric acid* produces in solutions containing nitrous acid, after neutralization by an acid of the free alkali, should any be present, a copious precipitate of sulphur, the reaction being attended also with formation of nitrate of ammonia. *Pyrogallic acid* imparts a brown color to even very dilute solutions of nitrites acidified with sulphuric acid (SCHÖNBEIN). On addition of *cyanide of potassium* to an alkaline nitrite, then of some neutral solution of *chloride of cobalt* and a little acetic acid, the fluid becomes orange-rose colored from the formation of nitrocyanide of cobalt and potassium (C. D. BRAUN). But the most delicate reagent for nitrous acid is solution of *iodide of potassium mixed with starch paste*, especially upon addition of sulphuric acid (PRICE, SCHÖNBEIN). Water containing the one hundred thousandth part of nitrite of potassa, together with free sulphuric acid, is colored distinctly blue by this reagent in a few seconds, and a few minutes suffice to produce the same effect in water containing one millionth part of nitrite of potassa. Let it be borne in mind that this reaction is reliable only where no other substance is present that might exercise a decomposing action upon iodide of potassium, such, for instance, as iodic acid, sesquioxide of iron, &c. On adding *indigo solution* to water till the latter has lost its transparence from the depth of color, then hydrochloric acid and afterwards a solution of *alkaline polysulphide* with stirring, till the blue color just vanishes, filtering and adding to the clear filtrate a solution of the merest trace of nitrous acid, a most distinct bluish coloration will at once be produced. This reaction is to be recommended in the presence of other reducing bodies which interfere with the action of nitrous acid upon an acidified solution of starch and iodide of potassium (SCHÖNBEIN). But it must not be overlooked that other oxidizing substances reproduce the blue color. On mixing a solution of nitrous acid (for instance, a solution of nitrite of potassa acidified with acetic acid) with *sulphocyanide of potassium*, the fluid is not colored, but on the further addition of nitric acid, a dark-red color makes its appearance, which vanishes on addition of alcohol or after heating for a short time (difference from sulphocyanide of iron). The coloring substance is mostly taken up,

* Journ. f. prakt. Chem. 78, 1. † Ann. d. Chem. u. Pharm. 107, 102.
‡ Zeitschr. f. anal. Chem. 4, 153.

from this by shaking with sulphide of carbon. It will be evident that this reaction is due to hyponitric acid and not to nitrous acid, hence it may be used to distinguish between the two.

### 2. Hypochlorous Acid (Cl O).

Hypochlorous acid, at the common temperature, is a deep yellowish-green gas of a disagreeable irritating odor, similar to that of chlorine. It dissolves in water; the dilute aqueous solution bears distillation. The hypochlorites are usually found in combination with metallic chlorides, as is the case, for instance, in chloride of lime, *eau de Javelle*, &c. The solutions of hypochlorites undergo alteration by boiling, the hypochlorite being resolved into chloride of the metal and chlorate of the oxide, attended, in the case of concentrated, but not in that of dilute solutions, with evolution of oxygen. If a solution of chloride of lime is mixed with hydrochloric acid or sulphuric acid, chlorine is disengaged, whilst addition of a little nitric acid leads to the liberation of hypochlorous acid. *Nitrate of silver* throws down from solution of chloride of lime chloride of silver [the hypochlorite of silver, which forms at first, is speedily resolved into chloride of silver and chlorate of silver: $3(Ag\,O, Cl\,O) = Ag\,O, Cl\,O_5 + 2\,Ag\,Cl$]: *nitrate of lead* produces a precipitate which from its original white changes gradually to orange-red, and ultimately, owing to formation of binoxide, to brown; *salts of protoxide of manganese* give brown-black precipitates of hydrate of binoxide of manganese. Solution of permanganate of potassa is not decolorized. Solutions of *litmus* and *indigo* are decolorized even by the alkaline solutions of hypochlorites, but still more rapidly and completely upon addition of an acid. If a solution of arsenious acid in hydrochloric acid is colored blue with solution of indigo, and a solution of chloride of lime is added, with active stirring, the decoloration will take place only after the whole of the arsenious acid has been converted into arsenic acid.

### 3. Chlorous Acid ($Cl\,O_3$).

Chlorous acid is a yellowish-green gas of a peculiar and very disagreeable odor; it is soluble in water. The solution has an intensely yellow color, even when highly dilute. Most of the chlorites are soluble in water; the solutions readily suffer decomposition, the chlorites being resolved into chlorides and chlorates. *Nitrate of silver* precipitates white chlorite of silver, which is soluble in much water. A solution of *permanganate of potassa* is immediately decomposed, and a brown precipitate separates after some time. *Tincture of litmus* and *solution of indigo* are instantly decolorized, even if mixed with arsenious acid in excess. If a slightly acidified dilute solution of a *salt of protoxide of iron* is mixed with a dilute solution of chlorous acid, the fluid transiently acquires an amethyst tint, and assumes only after the lapse of a few seconds the yellowish coloration of salts of sesquioxide of iron (Lenssen).

### 4. Hypophosphorous Acid (P O).

The concentrated solution of hypophosphorous acid is of syrupy consistence, and resembles that of phosphorous acid (see § 148), with which it also has this in common, that it is resolved by heating, with exclusion of air, into hydrate of phosphoric acid and not spontaneously inflammable phosphuretted hydrogen gas. Almost all hypophosphites are soluble in water; by ignition all of them are resolved into phosphate and phosphuretted hydrogen, which in most cases is spontaneously inflammable. *Chloride of barium*, *chloride of calcium*, and *acetate of lead* fail to precipitate solutions of hypophosphites (difference from phosphorous acid). *Nitrate of silver* gives with hypophosphites at first a white precipitate of hypophosphite of silver, which turns black even at the common temperature, but more rapidly on heating, the change of color being attended with separation of metallic silver. From *chloride of mercury* in excess hypophosphorous acid precipitates, slowly in the cold, more rapidly on heating, subchloride of mercury. With *zinc* and *dilute sulphuric acid* hypophosphorous acid gives hydrogen mixed with phosphuretted hydrogen. (Compare § 148, Phosphorous Acid.)

*Third Group.*

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTA NOR BY SALTS OF SILVER: *Nitric Acid, Chloric Acid* (Perchloric Acid).

## § 159.

### *a.* NITRIC ACID ($NO_5$).

1. ANHYDROUS NITRIC ACID crystallizes in six-sided prisms. It fuses at 29·5°, and boils at about 45° (DEVILLE). The pure HYDRATE is a colorless exceedingly corrosive fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous matter intensely yellow. Hydrate of nitric acid containing hyponitric acid has a red colour.

2. All the NEUTRAL SALTS of nitric acid are soluble in water; only some of the basic nitrates are insoluble. All nitrates undergo decomposition at an intense red heat. Those with alkaline bases at first yield oxygen, and change to nitrites, afterwards they yield oxygen and nitrogen. Those with other bases yield oxygen and nitrous or hyponitric acid.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion DEFLAGRATION takes place, *i.e.*, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

4. If a mixture of a nitrate with *cyanide of potassium* in powder is heated in small quantity on platinum foil, a vivid DEFLAGRATION ensues, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If a nitrate is mixed with *copper filings*, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitric oxide, which is liberated upon the oxidation of the copper by the nitric acid combining with the oxygen of the air to hyponitric acid. The coloration may be observed most distinctly by looking lengthways through the tube.

6. If the solution of a nitrate is mixed with an equal volume of concentrated *sulphuric acid*, free from nitric and hyponitric acid, the mixture allowed to cool, and a concentrated solution of *sulphate of protoxide of iron* then cautiously added to it so that the fluids do not mix, the junction shows at first a purple, afterwards a brown color, or, in cases where only a very minute quantity of nitric acid is present, a reddish color. On mixing the fluids a brownish purple-red *clear* fluid is obtained. In this process the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combining with the protoxide and converting a portion of it into sesquioxide, whilst the remaining nitric oxide combines with the remaining undecomposed salt of protoxide of iron, and forms with it a peculiar compound, which dissolves in water to a brownish-black color. A similar reaction is observed in presence of selenious acid; but on mixing the fluid, and letting it stand, red selenium separates (WITTSTOCK).

7. If some hydrochloric acid is boiled in a test-tube, one or two drops of very dilute *solution of sulphate of indigo* added, and the mixture

boiled again, the fluid remains blue (provided the hydrochloric acid was free from chlorine). If a nitrate, solid or in solution, is now added to the faint light-blue fluid, and the mixture heated again to boiling, the color disappears owing to the decomposition of the indigo blue. This is a most delicate reaction. It must be borne in mind, however, that several other substances also cause decoloration of solution of indigo—free chlorine more particularly produces this effect.

8. If a little *brucia* is dissolved in concentrated sulphuric acid, and a small quantity of a fluid containing nitric acid added to the solution, the latter immediately acquires a magnificent red color. This reaction is extraordinarily delicate. The color soon passes into reddish yellow. Chloric acid gives the same reaction.

9. Dissolve one part of *carbolic acid* in four parts of strong sulphuric acid, and add two parts of water. A drop or two of this fluid added to a solid nitrate (*e.g.*, to the residue obtained by evaporating a few drops of well-water containing nitrates) gives a reddish-brown color, from the formation of a nitro-compound. On addition of a drop or two of strong ammonia, this color turns yellow, sometimes passing through a green shade. A very delicate reaction (H. SPRENGEL).

10. Very minute quantities of nitric acid may be detected also by reducing the nitric acid first to nitrous acid, which may be effected both in the moist and in the dry way; in the former by heating the solution of the nitric acid or of the nitrate for some time with finely-divided zinc, best with zinc amalgam, and then filtering (SCHÖNBEIN); in the dry way by fusing the substance with carbonate of soda at a moderate heat, extracting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of iodide of potassium mixed with starch-paste and dilute sulphuric acid, the fluid acquires a blue color from iodide of starch (comp. § 158, 1).

## § 160.

### *b.* CHLORIC ACID ($ClO_3$).

1. CHLORIC ACID, in its most highly concentrated solution, is a colorless or slightly yellowish oily fluid; its odor resembles that of nitric acid. It first reddens litmus, then bleaches it. Dilute chloric acid is colorless and inodorous.

2. All CHLORATES are soluble in water. When chlorates are heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. Heated with *charcoal* or some organic substance the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with *cyanide of potassium* is heated on platinum foil, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. This experiment should be made with minute quantities only.

5. If the solution of a chlorate is colored light-blue with *solution of indigo*, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid

of its oxygen, thus setting free chlorine or a lower oxide of it, which then decolorizes the indigo.

6. If chlorates are heated with moderately dilute *hydrochloric acid* the constituents of the two acids transpose, forming water, chlorine, and $2\,Cl\,O_2$, $Cl\,O_4$. The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas of a very disagreeable odor resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow color. If the hydrochloric acid is colored blue with indigo solution, the presence of very minute quantities of chlorates will suffice to destroy the indigo color at once.

7. If a little chlorate is added to a few drops of *concentrated sulphuric acid* in a watch-glass, two-thirds of the metallic oxide are converted into sulphate, and the remaining one-third into perchlorate; this conversion is attended with liberation of chlorochloric acid, which imparts an intensely yellow tint to the sulphuric acid, and betrays its presence also by its odor and the greenish color of the evolved gas [$3(K\,O, Cl\,O_2) + 4(H\,O, S\,O_2) = 2(K\,O, H\,O, 2\,S\,O_2) + K\,O, Cl\,O_4 + (Cl\,O_2, Cl\,O_2) + 2\,H\,O$]. The application of heat must be avoided in this experiment, and the quantities operated upon should be very small, since otherwise the decomposition might take place with such violence as to cause an explosion.

8. Chloric acid shows the same deportment as nitric acid towards *brucia* dissolved in concentrated *sulphuric acid* (Luck). Compare § 159, 8.

## § 161.

*Recapitulation and remarks.*—Of the reactions which have been given to effect the detection of nitric acid, those with sulphate of protoxide of iron and sulphuric acid, with copper filings and sulphuric acid, with carbolic acid, and also those based upon the reduction to nitrites, give the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, decoloration of solution of indigo and coloration with brucia, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only where no chloric acid is present. The presence of free nitric acid in a fluid may be detected by evaporating in a porcelain dish on the water-bath to dryness, having first thrown in a few quill-cuttings: yellow coloration of these indicates the presence of nitric acid (Runge). The best way to ascertain whether chloric acid is present or not (in the absence of other oxygen compounds of chlorine) is to ignite the substance, with addition of carbonate of soda, dissolve the mass, and test the solution with nitrate of silver. If a chlorate is present, this is converted into a chloride upon ignition, and nitrate of silver will now produce a precipitate of chloride of silver. However, the process is thus simple only if no chloride is present with the chlorate. In presence of a chloride, the chlorine must be removed first by adding nitrate of silver to the solution as long as a precipitate continues to form, and filtering; the filtrate is then, after addition of pure carbonate of soda, evaporated and ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid, even in presence of nitrates.—The best way of

detecting nitric acid in presence of a large proportion of chloric acid is to mix the substance with carbonate of soda in excess, evaporate, ignite the residue gently, but sufficiently long to convert the chlorate into chloride, and then test the residue for nitric acid, or for nitrous acid.

§ 162.

PERCHLORIC ACID ($Cl O_7$).

Pure anhydrous perchloric acid is a colorless, mobile fluid, which forms dense white fumes in the air, and explodes with great violence when dropped on wood-charcoal (ROSCOE). The hydrate crystallizes in needles; the concentrated aqueous solution is oily and heavy. The dilute solution gives by distillation first water, then dilute acid, and finally concentrated acid. All perchlorates are soluble in water, most of them freely. They are all decomposed by ignition, those with alkaline bases leaving chlorides behind, with disengagement of oxygen. *Salts of potassa* produce in not too dilute solutions a white crystalline precipitate of perchlorate of potassa ($K O, Cl O_7$), which is sparingly soluble in water, insoluble in spirit of wine. *Baryta salts* and *silver salts* are not precipitated. Concentrated sulphuric acid fails to decompose perchloric acid in the cold, and decomposes it with difficulty on heating (difference from chloric acid). Hydrochloric acid, nitric acid, and sulphurous acid fail to decompose aqueous solutions of perchloric acid or perchlorates; solution of indigo, therefore, previously added to it, is not decolorized (difference from all other acids of chlorine).

## II. ORGANIC ACIDS.

### *First Group.*

THE HYDRATES OF THE ACIDS OF THE FIRST GROUP ARE DECOMPOSED ENTIRELY OR PARTIALLY BY IGNITION.* THE ACIDS ARE DECOMPOSED BY BOILING WITH CONCENTRATED NITRIC ACID.† THEIR LIME SALTS ARE INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER. THE SOLUTIONS OF THEIR NEUTRAL ALKALI SALTS ARE NOT PRECIPITATED BY SESQUICHLORIDE OF IRON: *Oxalic Acid, Tartaric Acid* (Racemic Acid), *Citric Acid, Malic Acid.*

§ 163.

*a.* OXALIC ACID.

For the reactions of oxalic acid I refer to § 145.

*b.* TARTARIC ACID ($2 H O, C_8 H_4 O_{10}$).

1. The HYDRATE OF TARTARIC ACID forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Heated to 100°, tartaric acid loses no water; heated to 170°, it fuses; at a higher temperature it becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar. Aqueous solution of tartaric acid, as also of almost all tartrates, turns the plane of polarization of light towards the right. By heating with nitric acid tartaric acid is converted into oxalic, acetic, and saccharic acids.

2. The TARTRATES with alkaline base are soluble in water, and so are those with the metallic oxides of the third and fourth groups. Evaporated on the water-bath to syrupy consistence, the solution of tartrate of sesquioxide of iron deposits a pulverulent basic salt. Those

* Hydrate of oxalic acid, when cautiously heated, partially sublimes unaltered.

† The decomposition of oxalic acid by boiling nitric acid into carbonic acid and water is but slow.

of the tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates, and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of an alkaline tartrate, solution of *sesquioxide of iron* or *alumina* is added in not too large proportion, and then ammonia or potassa, no precipitation of sesquioxide of iron or alumina will ensue, since the double tartrates formed are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other oxides by alkalies.

4. Free tartaric acid produces with *salts of potassa*, and more particularly with the acetate, a sparingly soluble precipitate of BITARTRATE OF POTASSA. A similar precipitate is formed when acetate of potassa and free acetic acid are added to the solution of a neutral tartrate. The acid tartrate of potassa dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The separation of the bitartrate of potassa precipitate is greatly promoted by shaking, or by rubbing the sides of the vessel with a glass rod. The delicacy of the reaction may be heightened by concentrating the solution of the tartaric acid. Addition of an equal volume of alcohol heightens the delicacy of the reaction. In the presence of boracic acid fluoride of potassium must be used instead of acetate of potassa, this forms borofluoride of potassium, and prevents the production of the soluble compound of boracic acid, tartaric acid, and potassa (BARFOED).

5. *Chloride of calcium* added in excess* throws down from solutions of neutral tartrates a white precipitate of TARTRATE OF LIME ($2\,CaO, C_8H_4O_{10} + 8\,aq.$). Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid or friction on the sides of the vessel promotes the separation of the precipitate. The precipitate is crystalline, or invariably becomes so after some time; it dissolves in a cold not over dilute solution of potassa or soda, pretty free from carbonic acid, to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* added in excess* produces in solutions of neutral tartrates—and also in a solution of free tartaric acid, if added to alkaline reaction—white precipitates which, flocculent at first, assume afterwards a crystalline form; so long as they remain flocculent they are readily dissolved by tartaric acid as well as by solution of chloride of ammonium. From these solutions the tartrate of lime separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of sulphate of lime* added in excess* fails to produce a precipitate in a solution of tartaric acid; in solutions of neutral tartrates of the alkalies, it produces a trifling precipitate after the lapse of some time.

8. If solution of ammonia is poured upon even a very minute quantity of tartrate of lime, a small fragment of crystallized *nitrate of silver*

* Tartrate of potassa or soda dissolves tartrate of lime (as well as certain other salts insoluble in water, such as phosphate of lime, sulphate of baryta, &c.). Hence the alkaline tartrate must be fully decomposed by the reagent.

added, and the mixture slowly and gradually heated, the sides of the test-tube are covered with a bright coating of metallic silver. If, instead of a crystal, solution of nitrate of silver be used, or heat be applied more rapidly, the reduced silver will separate in a pulverulent form (ARTHUR CASSELMANN).

9. *Acetate of lead* produces white precipitates in solutions of tartaric acid and its salts. The washed precipitate ($2\,Pb\,O, C_8 H_4 O_{10}$) dissolves readily in nitric acid and in ammonia free from carbonic acid.

10. *Nitrate of silver* does not precipitate free tartaric acid; but in solutions of neutral tartrates it produces a white precipitate of TARTRATE OF SILVER ($2\,Ag\,O, C_8 H_4 O_{10}$), which dissolves readily in nitric acid and in ammonia; upon boiling it turns black, owing to reduction of the silver.

11. Upon heating hydrated tartaric acid or a tartrate with *hydrate of sulphuric acid*, the latter acquires a brown color almost simultaneously with the evolution of gas.

## § 164.

### *c.* CITRIC ACID ($3\,H\,O, C_{12} H_5 O_{11}$).

1. CRYSTALLIZED CITRIC ACID, obtained by the cooling of its solution, has the formula $3\,H\,O, C_{12} H_5 O_{11} + 2$ aq. It crystallizes in pellucid, colorless and inodorous crystals of an agreeable strongly acid taste, which dissolve readily in water and in spirit of wine, and effloresce slowly in the air. Heated to 100° the crystallized acid loses its water of crystallization; when subjected to the action of a stronger heat, it fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization. By heating with a little nitric acid, citric acid gives oxalic and acetic acids, with much nitric acid it gives acetic acid only.

2. The CITRATES with alkaline base are readily soluble in water, as well in the neutral as in the acid state; solution of citric acid therefore is not precipitated by acetate of potassa. The compounds of citric acid with such of the metallic oxides as are weak bases, sesquioxide of iron, for instance, are also freely soluble in water. Evaporated on the water-bath to syrupy consistence the solution of citrate of sesquioxide of iron deposits no solid salt. Citrates, like tartrates, and for the same reason, prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of NEUTRAL CITRATE OF LIME ($3\,Ca\,O, C_{12} H_5 O_{11} + 4$ aq.) forms immediately upon saturating with potassa or soda the concentrated solution of citric acid, mixed with chloride of calcium in excess.* The precipitate is insoluble in potassa, but dissolves freely in solution of chloride of ammonium; upon boiling this chloride of ammonium solution, neutral citrate of lime of the same composition separates again in the form of a white crystalline precipitate, which however is now no longer soluble in chloride of ammonium. If a solution of citric acid mixed with excess of chloride of calcium* is saturated with ammonia, a precipitate will form in the cold only after

* Alkaline citrates are actual solvents for many compounds insoluble in water (sulphate of baryta, phosphate of lime, oxalate of lime, &c.). Hence the alkaline citrate must be fully decomposed by the reagent.

many hours' standing; but upon boiling the clear fluid, neutral citrate of lime of the properties just stated will suddenly precipitate. By heating citrate of lime with ammonia and nitrate of silver the latter salt is not reduced, or only to a trifling extent.

4. *Lime-water* added in excess* produces no precipitate in cold solutions of citric acid or of citrates. But upon boiling some time with a tolerable excess of hot prepared lime-water, a white precipitate of CITRATE OF LIME is formed, of which the greater portion redissolves upon cooling.

5. *Acetate of baryta* added in excess to a soluion of an alkaline citrate whether hot or cold, produces an amorphous precipitate of the formula $3\,BaO, C_{12}H_8O_{11} + 7$ aq. Baryta water added in excess to citric acid produces the same precipitate. The precipitate does not make its appearance in dilute solutions, because it is not insoluble in water, but if such solutions are heated, a precipitate separates which is first amorphous and soon turns to microscopic needles of the formula $3\,BaO, C_{12}H_8O_{11} + 5$ aq. On heating this or the amorphous salt with excess of acetate of baryta for two hours on the water-bath, another very characteristic salt is formed. The latter consists of well-formed clinorhombic prisms, and has the formula $2\,(3\,BaO, C_{12}H_8O_{11}) + 7$ aq. If the solution is very dilute the salt does not form till after evaporation. This is an infallible reaction for citric acid (H. KÄMMERER). From experiments made in my laboratory it appears that the addition of a drop of acetic acid materially assists the transition to the characteristic salt.

6. *Acetate of lead* added in excess to a solution of citric acid produces a white amorphous precipitate of CITRATE OF LEAD, which after washing is readily soluble in ammonia free from carbonic acid. By digestion for several hours with water or acetic acid on a water-bath, the precipitate becomes crystalline, and then has the formula $3\,PbO, C_{12}H_8O_{11} + 3$ aq. The microscope does not reveal the presence of well-formed crystals.

7. *Nitrate of silver* produces in solutions of neutral citrates of the alkalies a white flocculent precipitate of CITRATE OF SILVER ($3\,AgO, C_{12}H_8O_{11}$). On boiling a rather large quantity of this precipitate with a little water a gradual decomposition sets in with separation of silver.

8. Upon heating citric acid or citrates with concentrated *sulphuric acid*, carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural color; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

## § 165.

### *d.* MALIC ACID ($2\,HO, C_8H_4O_8$).

1. HYDRATE OF MALIC ACID crystallizes with great difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Exposed to a temperature of 150°, hydrated malic acid is slowly converted, with loss of two equivalents of water, into hydrated fumaric acid ($2\,HO, C_8H_2O_6$); heated to 180°, malic acid is resolved into water, MALEIC ACID ($2\,HO, C_8H_2O_6$), which volatilizes, and FUMARIC ACID ($2\,HO, C_8H_2O_6$), which remains. By raising the temperature to above 200° the fumaric acid is finally also volatilized. This deportment of malic acid is highly characteristic. If the

* See note, *ante*.

experiment is made in a small spoon, pungent acid vapors are evolved with frothing; if the experiment is made in a small tube, the maleic acid first, and afterwards the fumaric acid also will condense to crystals in the colder part of the tube. By heating with nitric acid malic acid readily yields oxalic acid, with evolution of carbonic acid.

2. Malic acid forms with most bases salts soluble in water. The acid malate of potassa is not difficultly soluble in water; acetate of potassa fails therefore to precipitate solutions of malic acid. Malic acid prevents, like tartaric acid, the precipitation of sesquioxide of iron, &c., by alkalies.

3. *Chloride of calcium* added in excess fails to produce a precipitate in solutions of free malic acid. Even after saturation with ammonia or soda no precipitate is formed. But upon boiling, a precipitate of MALATE OF LIME ($2\,CaO, C_8H_4O_8 + 6$ aq.) separates from concentrated solutions. If the precipitate is dissolved in a very little hydrochloric acid, ammonia added to the solution, and the fluid boiled, the malate of lime separates again; but if it is dissolved in a somewhat larger quantity of hydrochloric acid, it will not reprecipitate, after addition of ammonia in excess, even upon continued boiling. On adding one or two measures of alcohol the malate of lime separates in white flocks. If the fluid is previously heated nearly to boiling and hot alcohol is added, the precipitate is deposited in the form of soft lumps which adhere to the sides of the vessel; on cooling they harden and crumble by pressure to a crystalline powder (BARFOED). When heated with ammonia and nitrate of silver, malate of lime causes no separation of silver or hardly any.

4. *Lime-water* produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid remains perfectly clear even upon boiling, provided the lime-water was prepared with boiling water.

5. *Acetate of lead* throws down from solutions of malic acid and of malates a white precipitate of MALATE OF LEAD ($2\,PbO, C_8H_4O_8 + 6$ aq.). The precipitation is the most complete if the fluid is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the fluid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, and the remainder fuses to a mass resembling resin melted under water. To obtain this reaction with small quantities, warm at first gently till the precipitate has shrunk together, then pour off the principal quantity of the fluid and heat the rest with the precipitate to boiling. This reaction is distinctly marked only if the malate of lead is tolerably pure; if mixed with other salts of lead—if, for instance, ammonia is added to alkaline reaction—it is only imperfect or fails altogether to make its appearance.

6. *Nitrate of silver* throws down from solutions of neutral malates of the alkalies a white precipitate of MALATE OF SILVER, which upon long standing or boiling turns a little gray.

7. On mixing the warm solution of free malic acid with *magnesia* or its carbonate, till the acid reaction is destroyed, filtering, evaporating, and mixing the hot solution with hot alcohol, malate of magnesia ($2\,MgO, C_8H_4O_8$) separates as a glutinous mass on the sides of the vessel. It is hard when cold. Malic acid cannot be distinguished from citric acid by this reaction (BARFOED).

8. Upon heating malic acid with concentrated *sulphuric acid*, carbonic acid and carbonic oxide are evolved at first; the fluid then turns brown and ultimately black, with evolution of sulphurous acid.

§ 166.

*Recapitulation and remarks.*—Of the organic acids of this group *oxalic acid* is characterized by the instant precipitation of its lime-salt from its solution in hydrochloric acid by ammonia, and also by acetate of soda, as well as by the immediate precipitation of the free acid by solution of sulphate of lime. *Tartaric acid* is characterized by the sparing solubility of the acid potassa salt, the solubility of the lime-salt in cold solution of soda and of potassa, the reaction of the lime-salt with ammonia and nitrate of silver, and the peculiar odor which the acid and its salts emit upon heating. It is most safely detected in presence of the other acids by means of acetate of potassa or fluoride of potassium (§ 163, 4). C. D. BRAUN'S test for distinguishing tartaric acid from the other organic acids by means of hexamincobaltic chloride will be found in Zeitsch. f. anal. Chem. 7, 349. *Citric acid* is usually recognised by its reaction with lime water, or with chloride of calcium and ammonia in presence of chloride of ammonium; but in this we always presuppose the absence or the removal of malic and tartaric acids, and also the employment of a sufficient quantity of lime water or chloride of calcium. A very safe characteristic of citric acid also consists in the microscopic appearance of its baryta salt (§ 164, 5). *Malic acid* would be sufficiently characterized by the deportment of malate of lead when heated under water, were this reaction more sensitive, and not so easily prevented by the presence of other acids. The safest means of identifying malic acid is to convert it into maleic acid and fumaric acid by heating in a glass tube; but this conversion can be effected successfully only with pure hydrate of malic acid. Malate of lead is sparingly soluble in ammonia, whilst the citrate and tartrate of lead dissolve freely in that agent; this different deportment of the lead salts of the acids affords a means of distinguishing between them.

If only one of the four acids is present in a solution, lime-water will suffice to indicate which of the four is present; since malic acid is not precipitated by this reagent, citric acid is precipitated only upon boiling, tartaric acid and oxalic acid being thrown down in the cold; and the tartrate of lime redissolves upon addition of chloride of ammonium, whilst the oxalate does not.

If the four acids together are present in a solution, the oxalic acid and tartaric acid are usually precipitated first by chloride of calcium and ammonia, in presence of chloride of ammonium. But it must be noted here that the tartrate of lime requires some time for complete precipitation (it is separated from the oxalate by solution of soda), and also that alkaline citrate when present in any quantity prevents the thorough separation of oxalic acid and still more of tartaric acid. On adding alcohol in moderate quantity cautiously to the filtrate, the citrate of lime separates, (and with it the rest of the oxalate and tartrate of lime.) On filtering again and mixing the filtrate with more alcohol, the malate of lime is thrown down. From this the hydrated acid is prepared by dissolving it in acetic acid, adding alcohol, filtering if necessary, mixing the filtrate with acetate of lead, neutralizing with ammonia, washing the precipitate, suspending it in water, treating with sulphuretted hydrogen, filtering and evaporating the filtrate to dryness. A better method for the detection of malic acid in the presence of the three other acids consists in combining the acids with ammonia, concentrating

strongly, neutralizing the still warm fluid with ammonia (to dissolve the acid salts produced in the evaporation), and adding 8 volumes of alcohol of 98 per cent. After 12 or 24 hours the solution of malate of ammonia is filtered from the undissolved oxalate, tartrate, and citrate of ammonia, the malic acid is precipitated with acetate of lead and the pure hydrated acid is prepared from the precipitate (BARFOED). Where a small quantity of citric acid or malic acid is to be detected in presence of a large proportion of tartaric acid, the best way is to remove the latter first by acetate of potassa, with addition of an equal volume of strong alcohol. The other acids may then be completely precipitated in the filtrate by excess of chloride of calcium and ammonia if the quantity of the alcohol is a little increased.

§ 167.

RACEMIC ACID ($2\,H\,O, C_8H_4O_{10}$).

The formula of CRYSTALLIZED RACEMIC ACID is $2\,H\,O, C_8H_4O_{10} + 2$ aq. The crystallization water escapes slowly in the air, but rapidly at 100° (difference between racemic acid and tartaric acid). To solvents the racemic acid comports itself like the tartaric acid. The RACEMATES also show very similar deportment to that of the tartrates. However, many of them differ in the amount of water they contain, and in form and solubility from the corresponding tartrates. The aqueous solution of racemic acid and the racemates exercises no diverting action upon polarized light. *Chloride of calcium* precipitates from the solutions of free racemic acid and of racemates RACEMATE OF LIME ($2\,Ca\,O, C_8H_4O_{10} + 8$ aq.), as a white crystalline powder. Ammonia throws down the precipitate from its solution in hydrochloric acid, either immediately or at least very speedily (difference between racemic acid and tartaric acid). It dissolves in solution of soda and potassa, but is reprecipitated from this solution by boiling (difference between racemic acid and oxalic acid). *Lime-water* added in excess produces immediately a white precipitate insoluble in chloride of ammonium (difference between racemic and tartaric acid). *Solution of sulphate of lime* does not immediately produce a precipitate in a solution of racemic acid (difference between racemic and oxalic acid); however, after ten or fifteen minutes, racemate of lime separates (difference between racemic acid and tartaric acid); in solutions of neutral racemates the precipitate forms immediately. With *salts of potassa* racemic acid comports itself like tartaric acid. By letting racemate of soda and potassa or soda and ammonia crystallize, two kinds of crystals are obtained, which resemble each other as the image reflected by the mirror resembles the object reflected. The one kind of crystals contain common tartaric acid (which turns the plane of polarized light towards the right); the other kind contains antitartaric acid, i.e. an acid which is the same in every respect as tartaric acid, with this exception only, that it turns the polarized light towards the left. If the two kinds of crystals are redissolved, the solution shows again the reactions of racemic acid.

*Second Group.*

THE HYDRATES OF THE ACIDS OF THE SECOND GROUP SUBLIME WITHOUT ALTERATION. BY HEATING WITH NITRIC ACID THEY ARE EITHER LEFT UNCHANGED (SUCCINIC ACID), OR MERELY CONVERTED INTO NITRO-ACID (BENZOIC ACID). THE LIME-SALTS ARE READILY SOLUBLE IN WATER (BENZOIC ACID), OR DIFFICULTLY SOLUBLE (SUCCINIC ACID). THE SOLUTIONS OF THE NEUTRAL ALKALI-SALTS ARE PRECIPITATED BY SESQUICHLORIDE OF IRON: *Succinic Acid, Benzoic Acid.*

§ 168.

*a.* SUCCINIC ACID ($2\,H\,O, C_8H_4O_6$).

1. HYDRATE OF SUCCINIC ACID forms colorless and inodorous prisms or tables (rhombic prisms or rhomboid tables). It has a slightly acid

taste, is readily soluble in water and alcohol, slightly soluble in ether, difficultly soluble in nitric acid, and volatilizes when exposed to the action of heat, leaving only a little charcoal behind. The officinal acid has an empyreumatic odor, and leaves a somewhat larger carbonaceous residue upon volatilization. Succinic acid is not destroyed by heating with nitric acid, and may therefore be easily obtained in the pure state by boiling with that acid for half an hour, by which means the oil of amber, if present, will be destroyed. By sublimation crystalline needles of silky lustre are obtained. The hydrate loses water in this process, so that by repeated sublimation anhydrous acid is ultimately obtained. Heated in the air succinic acid burns with a blue flame, free from soot.

2. The SUCCINATES are decomposed at a red heat; those which have an alkali or alkaline earth for base are converted into carbonates with separation of charcoal. Most of the succinates are soluble in water. The succinate of soda is scarcely soluble in strong alcohol and crystallizes well both as a neutral and acid salt; hence it may be readily obtained in a pure state from very impure fluids. This property may be utilized for the detection and separation of the acid.* On heating the succinates with bisulphate of potassa in a tube the acid sublimes. The acid may also be obtained from the salts by decomposing them with sulphuric acid, and extracting with warm absolute alcohol.

3. On mixing a cold neutral moderately dilute solution of an alkaline succinate with *chloride of calcium*, no precipitate is formed; on then adding alcohol a gelatinous precipitate of SUCCINATE OF LIME falls, readily soluble in chloride of ammonium. From this solution more alcohol reprecipitates the gelatinous salt; in case of great dilution no precipitate is produced at first, but in a short time the succinate of lime separates in the crystalline form ($2\,CaO, C_8H_4O_6 + 6$ aq.).

4. *Sesquichloride of iron* produces in solutions of neutral succinates of the alkalies a brownish pale red bulky precipitate of SUCCINATE OF SESQUIOXIDE OF IRON ($Fe_2O_3, C_8H_4O_6$); one-third of the succinic acid is liberated in this reaction, and retains part of the precipitate in solution if the fluid is filtered off hot. The precipitate dissolves readily in mineral acids; ammonia decomposes it, causing the separation of a less bulky precipitate of a highly basic succinate of sesquioxide of iron, and combining with the greater portion of the acid to succinate of ammonia, which dissolves.

5. *Acetate of lead*, when added drop by drop to a solution of free succinic acid, or of an alkaline succinate, produces a white amorphous precipitate which is immediately redissolved in excess of succinic acid, in alkaline succinate, and in acetate of lead, but in a short time separates from such solutions in the crystalline form. The precipitate consists of neutral SUCCINATE OF LEAD ($2\,PbO, C_8H_4O_6$); it is barely soluble in water, acetic acid, succinic acid, and acetate of lead, readily soluble in nitric acid; by ammonia it is converted into a basic salt ($6\,PbO, C_8H_4O_6$).

6. A mixture of *alcohol, ammonia*, and *chloride of barium* produces in solutions of free succinic acid and of succinates a white precipitate of SUCCINATE OF BARYTA ($2\,BaO, C_8H_4O_6$).

* Compare MEISSNER and JOLLY, Zeitschr. f. anal. Chem. 4, 502.

## § 169.

### *b.* Benzoic Acid ($HO, C_{14}H_5O_3$).

1. Pure HYDRATE OF BENZOIC ACID forms inodorous white scales or needles, or simply a crystalline powder. It fuses when heated, and afterwards volatilizes completely. The fumes cause a peculiar irritating sensation in the throat, and provoke coughing; when cautiously cooled, they condense to brilliant needles; when kindled, they burn with a luminous sooty flame. The common officinal hydrate of benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Hydrate of benzoic acid is very sparingly soluble in cold water, but it dissolves pretty freely in hot water and in alcohol. Addition of water imparts therefore a milky turbidity to a saturated solution of the acid in alcohol.

2. Most of the BENZOATES are soluble in water; only those with weak bases, *e.g.*, sesquioxide of iron, are insoluble. The soluble benzoates have a peculiar pungent taste. The addition of a *strong acid* to concentrated aqueous solutions of benzoates displaces the benzoic acid, which separates as hydrate in the form of a dazzling white sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. *Sesquichloride of iron* precipitates solutions of free benzoic acid incompletely; solutions of neutral benzoates of the alkalies completely. The precipitate of BENZOATE OF SESQUIOXIDE OF IRON [$2Fe_2O_3$, $3(C_{14}H_5O_3) + 15$ aq.], is bulky, flesh-coloured, insoluble in water. It is decomposed by ammonia in the same manner as succinate of sesquioxide of iron, from which salt it differs in this, that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid.

4. *Acetate of lead* fails to precipitate free benzoic acid, but it produces flocculent precipitates in solutions of alkaline benzoates. The precipitate is insoluble in benzoate of soda, but dissolves in acetate of lead.

5. A mixture of *alcohol*, *ammonia*, and *chloride of barium*, or *chloride of calcium* produces no precipitate in solutions of benzoic acid or of the alkaline benzoates.

## § 170.

*Recapitulation and remarks.*—Succinic and benzoic acids are distinguished from one another by the color of their salts with sesquioxide of iron, and also by their different deportment with chloride of barium or chloride of calcium and alcohol; but principally by their different degrees of solubility, succinic acid being readily soluble in water, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore often be detected by the odor of oil of amber which it emits.

The detection of the two acids, when present in the same solution with other acids, may be effected as follows: precipitate with sesquichloride of iron, warm the washed precipitate with ammonia, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with chloride of barium and alcohol.

Succinic acid and benzoic acid do not prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

*Third Group.*

THE HYDRATES OF THE ACIDS OF THE THIRD GROUP MAY BE DISTILLED WITH WATER (THE HYDRATE OF LACTIC ACID WITH DIFFICULTY). THE LIME-SALTS ARE READILY SOLUBLE IN WATER. THE SOLUTIONS OF THE NEUTRAL ALKALINE-SALTS ARE NOT PRECIPITATED IN THE COLD BY SESQUICHLORIDE OF IRON: *Acetic Acid, Formic acid* (Lactic Acid, Propionic Acid, Butyric Acid).

## § 171.

### *a.* ACETIC ACID ($HO, O_4H_3O_3$).

1. The HYDRATE OF ACETIC ACID forms transparent crystalline scales, which fuse at 17° to a colorless fluid of a peculiar pungent and penetrating odor, and exceedingly acid taste. When exposed to the action of heat it volatilizes completely, forming pungent vapors, which burn with a blue flame. It is miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The ACETATES undergo decomposition at a red heat; among the products of this decomposition we generally find hydrate of acetic acid, and almost invariably acetone ($C_3H_6O_2$). The acetates of the alkalies and alkaline earths are converted into carbonates in this process; of the acetates with metallic bases many leave the metal behind in the pure state, others in the form of oxide. Most of the residues which the acetates leave upon ignition are carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in that menstruum. If acetates are distilled with dilute sulphuric acid, the free acetic acid is obtained in the distillate.

3. If *sesquichloride of iron* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with sesquichloride of iron, the fluid acquires a deep red color, owing to the formation of ACETATE OF SESQUIOXIDE OF IRON. By boiling the fluid becomes colorless if it contains an excess of acetate, the whole of the sesquioxide of iron precipitating as a basic acetate, in the form of brown-yellow flakes. Ammonia precipitates from it the whole of the sesquioxide of iron as hydrate. By addition of hydrochloric acid a fluid which appears red from the presence of acetate of sesquioxide of iron turns yellow (difference from sulphocyanide of iron).

4. Neutral acetates (but not free acetic acid of a certain degree of dilution) give with *nitrate of silver* white crystalline precipitates of ACETATE OF SILVER ($AgO, C_4H_3O_3$), which are very sparingly soluble in cold water. They dissolve more easily in hot water, but separate again upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Nitrate of suboxide of mercury* produces in acetic acid, and more

readily still in acetates, white scaly crystalline precipitates of ACETATE OF SUBOXIDE OF MERCURY ($Hg_2O, C_4H_3O_3$), which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water upon heating, but separate again upon cooling, in the form of small crystals; in this process the salt undergoes partial decomposition: a portion of the mercury separates in the metallic state, and imparts a gray color to the precipitate. If the acetate of suboxide of mercury is boiled with dilute acetic acid, instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. *Chloride of mercury* produces no precipitate of subchloride of mercury with acetic acid or acetates upon heating.

7. By heating acetates with *concentrated sulphuric acid* HYDRATE OF ACETIC ACID is evolved, which may be known by its pungent odor. But if the acetates are heated with a mixture of about equal volumes of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER ($C_4H_5O, C_4H_3O_3$) is formed. The odor of this ether is highly characteristic and agreeable; it is most distinct upon shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odor of the acid.

8. If dilute acetic acid is heated with an excess of *oxide of lead*, part of the latter dissolves as basic acetate of lead. The fluid has an alkaline reaction: it gives no crystals on cooling.

## § 172.

### *b.* FORMIC ACID ($HO, C_2HO_3$).

1. The HYDRATE OF FORMIC ACID is a transparent and colorless slightly fuming liquid of a characteristic and exceedingly penetrating odor. When cooled to below 0°, it crystallizes in colorless plates. It is miscible in all proportions with water and alcohol. When exposed to the action of heat, it volatilizes completely; the vapors burn with a blue flame.

2. The FORMATES, like the corresponding acetates, leave upon ignition either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and escape of carbide of hydrogen, carbonic acid, and water. All the compounds of formic acid with bases are soluble in water; alcohol also dissolves many of them but not all.

3. Formic acid shows the same reaction with *sesquichloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and decomposes the alkaline formates only in concentrated solutions. The white sparingly soluble, crystalline precipitate of FORMATE OF SILVER ($AgO, C_2HO_3$) acquires very rapidly a darker tint, owing to the separation of metallic silver. Complete reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time; but immediately upon applying heat to the fluid containing the precipitate. The same reduction of the oxide of silver to the metallic state takes place in a solution of free formic acid, and also in solutions of formates so dilute that the addition of the nitrate of silver fails to produce a precipitate. But it does not take place in presence of an excess of am-

monia. The rationale of this reduction is as follows: the formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, thus causing the formation of carbonic acid, which escapes, and of water, whilst the reduced silver separates.

5. *Nitrate of suboxide of mercury* gives no precipitate with free formic acid: but in solutions of alkaline formates this reagent produces a glistening white sparingly soluble precipitate of FORMATE OF SUBOXIDE OF MERCURY ($Hg_2O, C_2HO_3$), which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction is also attended with the formation of carbonic acid and water, and takes place, as with the oxide of silver, both in solutions of free formic acid and in fluids so highly dilute that the formate of suboxide of mercury is retained in solution.

6. If formic acid or an alkaline formate is heated with *chloride of mercury* to between 60° and 70° SUBCHLORIDE OF MERCURY precipitates. Presence of free hydrochloric acid or of somewhat considerable quantities of alkaline chlorides prevents the reaction.

7. If formic acid or a formate is heated with *concentrated sulphuric acid* the formic acid is resolved into water and carbonic oxide gas, which latter escapes with effervescence and, if kindled, burns with a blue flame. The fluid does not turn black in this process. The rationale of the decomposition of the formic acid is this: the sulphuric acid withdraws from the formic acid the water or the oxide necessary for its existence, and thus occasions a transposition of its elements ($C_2HO_3 = 2CO + HO$). Upon heating formates with dilute sulphuric acid in a distilling apparatus free formic acid is obtained in the distillate, and may mostly be readily detected by its odor. Upon heating a formate with a mixture of strong sulphuric acid and alcohol formic ether is evolved, which is characterized by its peculiar arrack-like smell.

8. If dilute formic acid is heated with excess of *oxide of lead*, the latter partially dissolves. The fluid has an alkaline reaction. On cooling the solution, which, if necessary, is concentrated by evaporation, the FORMATE OF LEAD ($PbO, C_2HO_3$) separates in brilliant prisms or needles.

## § 173.

*Recapitulation and remarks.*—Acetic acid and formic acid may be distilled over with water, and form with sesquioxide of iron soluble neutral salts which dissolve in water, with a blood-red color, and are decomposed upon boiling. These reactions distinguish the two acids of the third group from the other organic acids. From each other the two acids are distinguished by the odor of their hydrates and ethyle compounds, and by their different reactions with salts of silver and salts of mercury, oxide of lead, and concentrated sulphuric acid. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of oxide of mercury or oxide of silver. Formic acid reduces the oxide, and suffers decomposition, whilst the acetic acid combines with the oxide, and remains in solution.

## § 174.

### *Rarer Acids of the third group.*

#### 1. Lactic Acid ($2HO, C_{12}H_{10}O_{10}$).

Lactic acid is developed in animal fluids, vegetable matters that have turned sour, &c. Pure hydrate of lactic acid is an inodorous syrupy liquid; it has a pure acid, sharp taste. When it is slowly heated in a retort to 130°, water containing a little hydrated lactic acid distils over, leaving a residue of anhydrous lactic acid ($C_{12}H_{10}O_{10}$), which between 250° and 300° is decomposed into carbonic oxide, carbonic acid, lactide, and other products. Hydrate of lactic acid dissolves freely in water, alcohol, and ether. Upon boiling the aqueous solution a little lactic acid volatilizes with the aqueous vapour. All the lactates are soluble in water, the greater part of them, however, only sparingly; it is the same with regard to spirit of wine; they are all insoluble in ether. The production of some of these salts and the examination of their form under the microscope supply the means for the detection of lactic acid; lactate of lime and lactate of zinc are the best suited for this purpose. Lactate of lime may be conveniently prepared from animal or vegetable juices by the following method devised by Scheeer:—Dilute the liquid, if necessary, with water, mix with baryta-water, and filter. Distil the filtrate with some sulphuric acid (to remove volatile acids), digest the residue several days with strong alcohol, distil the acid solution with a little milk of lime, filter warm from the excess of lime and the sulphate of lime, conduct carbonic acid into the filtrate, heat once more to boiling, filter from the precipitated carbonate of lime, evaporate the filtrate, warm the residue with strong alcohol, filter, and let the neutral filtrate stand several days to give the lactate of lime time to crystallize. Should the quantity of lactic acid present be insufficient to allow the formation of crystals, evaporate the fluid to syrupy consistence, mix with strong alcohol, let the mixture stand some time, decant or filter the alcoholic solution into a vessel that can be closed, and add gradually a small quantity of ether. This process will cause even minute traces of lactate of lime to separate from the fluid. Lactate of lime shows under the microscope the form of minute crystalline needles aggregated in tufts with short stalks, pairs of them always being joined at the stalked ends, so as to look like paint-brushes united together.—Lactate of zinc deposited quickly from its solution shows under the microscope the form of spherical groups of needles. The slow evaporation of solution of lactate of zinc gives first crystals resembling clubs truncated at both ends; these crystals gradually increase in size; the two ends apparently diminish, whilst the middle parts increase in size (Funke).

#### 2. Propionic Acid ($HO, C_6H_5O_3$), and 3. Butyric Acid ($HO, C_8H_7O_3$).

Propionic acid is formed under a great variety of circumstances; it is chiefly found in fermented liquids. The pure hydrate of the acid crystallizes in minute plates; it boils at 140—142°; it dissolves readily in water. Propionic acid floats as an oily stratum on aqueous solution of phosphoric acid and on solution of chloride of calcium. It has a peculiar smell, which reminds both of butyric and acetic acid. Upon distilling the aqueous solution, the propionic acid passes over into the distillate. Butyric acid is frequently found in animal and vegetable matter, more particularly also in fermented liquids of various kinds. The pure hydrate of the acid is a colorless, mobile, corrosive, intensely sour fluid, of a disagreeable odor, a combination of the smell of rancid butter and acetic acid; it boils at 160°. It is miscible in all proportions with water and alcohol. It is separated from the concentrated aqueous solution by chloride of calcium, concentrated acids, &c., in the form of a thin oil. The smell of butyric acid is particularly strong in the aqueous solution of the acid. Upon distilling the aqueous solution, the acid passes over with the aqueous vapors.

Propionic acid and butyric acid are often found associated with formic acid and acetic acid in fermented liquids, in guano, and in many mineral waters. The detection of the several acids may in such cases be effected as follows: dilute the substance sufficiently with water, acidify with sulphuric acid, and distil; saturate the distillate with baryta-water, evaporate to dryness, and treat the residue repeatedly with boiling alcohol of 85 per cent. This will leave the formate of baryta and part of the acetate, the remainder of the acetate, together with the propionate and butyrate, dissolving in the alcohol. Evaporate the alcoholic solution, dissolve the residue in water, decompose cautiously with sulphate of silver, boil, filter, and let the fluid (which ought rather to contain a little undecomposed baryta salt than any sulphate of silver) evaporate under the desiccator. Take out separately the crystals, which form first, those which

form after, and those which form last, and examine them to ascertain their nature. Acetate of silver emits upon solution in concentrated sulphuric acid the odor of acetic acid, and gives no oily drops; propionate and butyrate of silver emit the peculiar odor of the acids, and give oily drops, which, however, with minute quantities are visible only under the microscope. To distinguish positively between propionic and butyric acid, it is indispensable to determine the amount of silver in the separated silver salts, and to fix by this the atomic weight of the acids. If much acetate of baryta has passed into the solution, with a small quantity only of butyrate and propionate, the baryta is first exactly precipitated with sulphuric acid from the aqueous solution of the baryta salts soluble in alcohol, half of the acid fluid neutralized with soda, the other half added, the fluid then distilled, the distillate, which now contains principally propionic and butyric acids, saturated with baryta, then decomposed with sulphate of silver, and the remaining part of the process conducted as above.

# PART II.

# SYSTEMATIC COURSE

OF

# QUALITATIVE CHEMICAL ANALYSIS.

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## PRELIMINARY REMARKS

ON THE

### COURSE OF QUALITATIVE ANALYSIS IN GENERAL, AND ON THE PLAN OF THIS PART OF THE PRESENT WORK IN PARTICULAR.

THE knowledge of reagents and of the deportment of bodies with them enables us to ascertain at once whether a simple compound of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, a few simple reactions suffice to show that a body which appears to be calcareous spar is really carbonate of lime, and that another which we hold to be gypsum is actually sulphate of lime. This knowledge usually suffices also to ascertain whether a certain body is present or not in a mixture; for instance, whether or not a white powder contains subchloride of mercury. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover all the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected, no other substance can possibly be present—if consequently a complete qualitative analysis is our object, the mere knowledge of the reagents, and of the reactions of bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a systematic course of analysis, in other words, the knowledge of the order in which solvents, and general and special reagents, should be applied, both to effect the speedy and certain detection of every element present, and to prove with certainty the absence of all others. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method, analyzing becomes (at least in the hands of a novice) mere guess-work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a

due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances to be looked for are in the first place classed into groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a course of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will be best adapted to a given case.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the *First Section*.

The elements and compounds comprised in it are the same which we have studied in Part I., with the exception of those discussed more briefly, and marked by the use of smaller type.

The subdivisions of this systematic course are, 1, Preliminary Examination; 2, Solution; 3, Actual Examination.

The third subdivision (the *Actual Examination*) is again divided into (1) Examination of compounds in which but one base and one acid are assumed to be present; and (2) Examination of mixtures or compounds in which all the substances treated in the present work are assumed to be present. With respect to the latter I have to remark that where the preliminary examination has not clearly demonstrated the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made in consequence of the reactions observed. In cases where the intention is simply to test a mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

As the construction of a universally applicable systematic course of analysis requires due provision for every contingency that may possibly arise, it is self-evident that, though in the system here laid down the various bodies comprised in it have been assumed to be mixed up together in every conceivable way, it was absolutely indispensable to assume that no foreign organic matters were present, since the presence of such matters would introduce various complications.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, still there are special cases in which it may be advisable to modify it. A preliminary treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with; the presence of coloring or slimy organic matters more especially requires certain preliminary operations. The *Second Section* will be found to contain a detailed description of the special methods employed to meet certain cases which frequently occur. Some of these methods show how the analytical process becomes simplified as the number of substances decreases to which regard must be had.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depend, I have given in the *Third Section* an explanation of the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, I strongly recommend students to make themselves early and thoroughly acquainted with it. I have devoted a special section to this theoretical explanation, as I think it will be understood better in a connected form than it would have been by explanatory additions to the several paragraphs, which, moreover, might have materially interfered with the perspicuity of the practical process.

I have also in this third section taken occasion to point out in what residues, solutions, precipitates, &c., which are obtained in the systematic course of analysis, the more rarely occurring elements may be expected to be met with; and also to give instructions how to proceed with a view to ensure the detection of these bodies also systematically.

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# SECTION I.

## PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

### I. Preliminary Examination.*

§ 175.

**Examine**, in the first place, the external properties, such as the color, shape, hardness, gravity, odor, &c., of the substance, since these will often enable you in some measure to infer its nature. Before proceeding, if the quantity of the substance is limited, you must consider how much may safely be spared for the preliminary examination. A reasonable economy is in all cases advisable, even though you may possess the substance in large quantities; but, under all circumstances, let it be a fixed rule never to use up the whole of what you possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments. 1†

#### A. The Body under Examination is Solid.

##### I. It is neither a Metal nor an Alloy.

§ 176.

1. The substance is fit for examination if in powder or in minute crystals; but in the case of larger crystals or solid pieces, a portion must, if practicable, be first reduced to *fine powder*. Bodies of the softer kind may be triturated in a porcelain mortar; those of a harder 2

* Consult also the observations in the Third Section of Part II.

† These marginal numbers are simply intended to facilitate reference.

nature must first be broken into small pieces in a steel mortar; or upon a steel anvil, and the pieces then be triturated in an agate mortar.

2. PUT SOME OF THE POWDER INTO A GLASS TUBE, SEALED AT ONE END, ABOUT SIX CENTIMETRES LONG AND FIVE MILLIMETRES WIDE, AND HEAT first gently over the spirit or gas-lamp, then intensely in the blowpipe flame. The reactions resulting may lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; it often occurs that several of them are observed in the case of one and the same substance. 3

*a.* THE SUBSTANCE REMAINS UNALTERED: absence of organic matters, salts containing water of crystallization, readily fusible matters, and volatile bodies (except carbonic acid, which often escapes without visible change). 4

*b.* THE SUBSTANCE DOES NOT FUSE AT A MODERATE HEAT BUT SIMPLY CHANGES COLOR. From white to yellow, turning white again on cooling, indicates OXIDE OF ZINC; from white to yellowish brown, turning to a dirty light yellow on cooling, indicates BINOXIDE OF TIN; from white or yellowish-red to brownish-red, turning to yellow on cooling, the body fusing at a red heat, indicates OXIDE OF LEAD; from white, or pale yellow, to orange yellow, up to reddish-brown, turning pale yellow on cooling, the body fusing at an intense red heat, indicates TEROXIDE OF BISMUTH; from brownish-red to black, turning brownish-red again on cooling, indicates SESQUIOXIDE OF IRON; from yellow to dark orange, the body fusing at an intense heat, indicates NEUTRAL CHROMATE OF POTASSA, &c. 5

*c.* THE SUBSTANCE FUSES WITHOUT EXPULSION OF AQUEOUS VAPORS. If by intense heating, gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, NITRATES or CHLORATES are indicated. 6

*d.* AQUEOUS VAPORS ARE EXPELLED, WHICH CONDENSE IN THE COLDER PART OF THE TUBE: this indicates either (*α*) SUBSTANCES CONTAINING WATER OF CRYSTALLIZATION, in which case they will generally readily fuse, and re-solidify after expulsion of the water; many of these swell considerably whilst yielding up their water, *e.g.*, borax, alum; or (*β*) decomposable HYDRATES, in which case the bodies often will not fuse; or (*γ*) anhydrous salts, holding WATER MECHANICALLY ENCLOSED between their lamellæ, in which case the bodies will decrepitate; or (*δ*) bodies with MOISTURE externally adhering to them. 7

Test the reaction of the condensed fluid in the tube; if it is alkaline, ammonia is indicated; if acid, a volatile acid (sulphuric, sulphurous, hydrofluoric, hydrochloric, hydrobromic, hydriodic, nitric, &c).

*e.* GASES OR FUMES ESCAPE. Observe whether they have a color, a smell, an acid or alkaline reaction, whether they are inflammable, &c. 8

*aa.* OXYGEN indicates peroxides, chlorates, nitrates, &c. A glimmering slip of wood is relighted in the gaseous current.

*bb.* SULPHUROUS ACID is often produced by the decomposition of sulphates; it may be known by its odor and by its acid reaction.

*cc.* HYPONITRIC ACID, resulting from the decomposition of nitrates, especially those of the heavy metals; it may be known by the brownish-red color and the odor of the fumes.

*dd.* CARBONIC ACID indicates carbonates decomposable by heat, or oxalates of reducible metals. The gas is colorless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

*ee.* CARBONIC OXIDE indicates oxalates and also formates. The gas burns with a blue flame. In the case of oxalates the carbonic oxide is generally mixed with carbonic acid, and is therefore more difficult to kindle: in the case of formates there is marked carbonization. Oxalates evolve carbonic acid when brought into contact with binoxide of manganese, a little water, and some concentrated sulphuric acid, on a watch-glass; formates evolve no carbonic acid under similar circumstances.

*ff.* CHLORINE, BROMINE, OR IODINE indicate decomposable chlorides, bromides, or iodides. The gases are readily recognised by their color and odor. Iodine, if evolved in any quantity, forms a black sublimate (compare 9).

*gg.* CYANOGEN indicates cyanides decomposable by heat. The gas may be known by its odor, and, when tolerably pure, by the crimson flame with which it burns.

*hh.* HYDROSULPHURIC ACID indicates sulphides containing water; the gas may be readily known by its odor.

*ii.* AMMONIA, resulting from the decomposition of ammoniacal salts, or also of cyanides or nitrogenous organic matters, in which latter cases browning or carbonization takes place, and either cyanogen or offensive empyreumatic oils escape with the ammonia.

*f.* A SUBLIMATE FORMS. This indicates volatile bodies: 9
the following are those more frequently met with:—

*aa.* SULPHUR. Eliminated from mixtures or from many of the metallic sulphides. Sublimes in reddish-brown drops, which solidify on cooling, and turn yellow or yellowish-brown.

*bb.* IODINE. Eliminated from mixtures, many iodides, iodic acid, &c. Violet vapor, black sublimate, smell of iodine.

*cc.* AMMONIA SALTS give white sublimates; heated with carbonate of soda and a drop of water on platinum foil they evolve ammonia.

*dd.* MERCURY and its compounds. METALLIC MERCURY forms globules; SULPHIDE OF MERCURY is black, but acquires a red tint when rubbed; CHLORIDE OF MERCURY fuses before volatilizing; SUBCHLORIDE OF MERCURY sublimes without previous fusion, the sublimate, which is yellow whilst hot, turns white on cooling. The red IODIDE OF MERCURY gives a yellow sublimate.

*ee.* ARSENIC and its compounds. METALLIC ARSENIC

forms the well-known arsenical mirror; ARSENIOUS ACID forms small shining crystals; the SULPHIDES OF ARSENIC give sublimates which are reddish-yellow whilst hot, and turn yellow on cooling.

*ff.* TEROXIDE OF ANTIMONY fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

*gg.* BENZOIC ACID and SUCCINIC ACID. The officinal impure acids may be known by the odor of their fumes.

*hh.* HYDRATED OXALIC ACID. White crystalline sublimate, thick irritating fumes in the tube. Heating a small sample on platinum-foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

*g.* CARBONIZATION TAKES PLACE: organic substances. 10
This is always attended with evolution of gases (acetates evolve acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkalies or alkaline earths. Salts containing readily reducible metallic oxides in combination with organic acids, often leave the metal behind, and in consequence of the combustion of the carbon at the expense of the metallic oxide, the residue may contain little or no carbon.

3. PLACE A SMALL PORTION OF THE SUBSTANCE ON A CHAR- 11
COAL SUPPORT (in the cavity scooped out for the purpose), AND EXPOSE TO THE INNER BLOWPIPE FLAME.

As most of the reactions described under 2 (3—10) are also produced by this process, only those appearances will be mentioned which are peculiar to this experiment. Evolution of sulphurous acid, when the flame plays upon the sample, generally indicates a sulphide. The following are the reactions which will permit pretty accurate conclusions.

*a.* THE BODY FUSES, AND IS ABSORBED BY THE CHARCOAL 12
OR FORMS A BEAD IN THE CAVITY, not attended by incrustation: indicates more particularly salts of the alkalies.

*b.* AN INFUSIBLE WHITE RESIDUE REMAINS on the char- 13
coal, either at once or after previous melting in the water of crystallization; indicates more particularly baryta, strontia, lime, magnesia, alumina, oxide of zinc (appears yellow whilst hot), and silicic acid. Among these substances STRONTIA, LIME, MAGNESIA, and OXIDE OF ZINC are distinguished by strong luminosity in the blowpipe flame. Moisten the white residue with a drop of nitrate of cobalt, and expose again to a strong heat. A fine blue tint indicates ALUMINA; a green OXIDE OF ZINC. In the presence of SILICIC ACID and of many alkaline earthy PHOSPHATES a more or less blue coloration is produced.

In the case *a* or *b* the preliminary examination for alkalies and alkaline earths may be completed by inspecting the colors which the substances impart to flame. For this purpose a little of the substance is attached to the loop of a fine platinum wire, moistened repeatedly with sulphuric acid, dried cautiously near the border of the flame, and then held in the fusing zone of

BUNSEN'S gas-flame. The colorations caused by the alkalies will make their appearance first, followed—after volatilization of the alkalies, by that of baryta, and finally—after moistening with hydrochloric acid—by those of strontia and lime. For details see § 92 and § 99.

*c.* THE SUBSTANCE LEAVES A RESIDUE OF ANOTHER COLOR, OR REDUCTION TO THE METALLIC STATE TAKES PLACE, OR AN INCRUSTATION FORMS ON THE CHARCOAL. Mix a portion of the powder with carbonate of soda and a drop of water, and heat on charcoal in the reducing flame; observe the residue in the cavity as well as the incrustation on the charcoal. **14**

*a.* The sustained application of a strong flame produces a metallic globule, without incrustation of the charcoal, indicates GOLD OR COPPER. The latter is at once recognised by the green coloration of the flame. The oxides of platinum, iron, cobalt, and nickel are indeed also reduced, but they yield no metallic globules. **15**

*β.* The charcoal support is coated with an incrustation, either with or without formation of a metallic globule. **16**

*aa.* The incrustation is *white*, at some distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odor: ARSENIC.

*bb.* The incrustation is *white*, nearer the test specimen than in *aa*, and may be driven from one part of the support to another: ANTIMONY. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after the blowpipe jet is discontinued, and upon cooling become surrounded with crystals of teroxide of antimony; the globules are brittle.

*cc.* The incrustation is *yellow* whilst hot, but turns white on cooling; it is pretty near the test specimen and is with difficulty volatilized: ZINC.

*dd.* The incrustation has a *faint yellow* tint whilst hot, but turns white on cooling; it surrounds the test specimen closely, and both the inner and outer flame fail to volatilize it: TIN. The metallic globules formed at the same time, but only in a strong reducing flame, are bright, readily fusible, and malleable.

*ee.* The incrustation has a *lemon-yellow* color, turning on cooling to sulphur-yellow; heated in the reducing flame it leaves its place with a blue gleam: LEAD. Readily fusible, malleable globules are formed at the same time with the incrustation.

*ff.* The incrustation is of a *dark orange-yellow* color whilst hot, which changes to lemon-yellow on cooling; heated in the reducing flame it leaves its place without a blue gleam: BISMUTH. The metallic globules formed at the same time as the incrustation are readily fusible and brittle.

*gg.* The incrustation is reddish-brown, in thin layers orange-yellow; it volatilizes without a coloured gleam: CADMIUM.

*hh.* The incrustation is dark-red: SILVER Where lead

and antimony are present at the same time, the incrustation is crimson.

In cases where a reduction to the metallic state has taken place, moisten the sample with water, scoop it out, triturate in a small agate dish, and wash off the charcoal particles with water—when the gold will be obtained in yellow, the copper in coppery-red, the silver in nearly white, the tin in grayish-white, the lead in whitish-gray minute plates or strips, the bismuth as a reddish-gray, the zinc as a bluish-white, the antimony as a gray powder. When copper and tin, or copper and zinc, are present at the same time, yellow alloys are occasionally formed.

4. FUSE A SMALL PORTION WITH A BEAD OF MICROCOSMIC SALT, AND EXPOSE FOR SOME TIME TO THE OUTER FLAME OF THE BLOWPIPE. 17

*a.* THE SUBSTANCE DISSOLVES READILY AND RATHER COPIOUSLY TO A CLEAR BEAD (WHILST HOT).

*a. The hot bead is colored:* 18

BLUE, by candlelight inclining to violet—COBALT;

GREEN, upon cooling blue; in the reducing flame, after cooling, red—COPPER;

GREEN, particularly fine on cooling, unaltered in the reducing flame—CHROMIUM;

BROWNISH-RED, on cooling light yellow or colorless; in the reducing flame red whilst hot, yellow whilst cooling, then greenish—IRON;

REDDISH to BROWNISH-RED, on cooling yellow to reddish-yellow or colorless; in the reducing flame unaltered—NICKEL;

YELLOWISH-BROWN, on cooling light yellow or colorless; in the reducing flame almost colorless (especially after contact with tin), blackish-gray on cooling—BISMUTH.

LIGHT YELLOWISH to OPAL, when cold rather dull; in the reducing flame whitish-gray—SILVER:

AMETHYST-RED, especially on cooling; colorless in the reducing flame, not quite clear—MANGANESE.

*β. The hot bead is colorless:* 19

IT REMAINS CLEAR ON COOLING: ANTIMONY, ALUMINA, ZINC, CADMIUM, LEAD, LIME, MAGNESIA; the latter five when added in somewhat large proportion to the microcosmic salt, give enamel-white beads; the bead of oxide of lead saturated is yellowish;

IT BECOMES ENAMEL-WHITE ON COOLING, EVEN WHERE ONLY A SMALL PORTION OF THE POWDER HAS BEEN ADDED TO THE MICROCOSMIC SALT: BARYTA, STRONTIA.

*b.* THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY: 20

*a.* The bead is colorless, and remains so even after cooling; the undissolved portion looks semi-transparent; upon addition of a little sesquioxide of iron it acquires the characteristic color of an iron bead: SILICIC ACID.

*β.* The bead is colorless, and remains so after addition of a little sesquioxide of iron: TIN.

*c.* THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD: GOLD, PLATINUM. 21

5. MINERALS ARE EXAMINED FOR FLUORINE AS DIRECTED § 146, 8.

After the termination of the preliminary examination, proceed to the solution of the substance, as directed § 180 (32).

## § 177.

### II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. HEAT A SMALL PORTION OF THE SUBSTANCE WITH WATER ACIDULATED WITH ACETIC ACID. If HYDROGEN is evolved this indicates a light metal (possibly also manganese). 22

2. HEAT A SAMPLE OF THE SUBSTANCE ON CHARCOAL IN THE REDUCING FLAME OF THE BLOWPIPE, and watch the reactions; for instance, whether the substance fuses, whether an incrustation is formed, or an odor emitted, &c. 23

By this operation the following metals may be detected with more or less certainty: ARSENIC by the smell of garlic; MERCURY by its volatility; ANTIMONY, ZINC, LEAD, BISMUTH, CADMIUM, TIN, SILVER, by fusing, with incrustation of the charcoal (comp. 16); COPPER by the green coloration of the outer flame. Further conclusions may be formed when the substance is a single metal nearly pure; thus, for instance GOLD fuses without incrustation; PLATINUM, IRON, MANGANESE, NICKEL, and COBALT, do not fuse in the blowpipe flame.

3. HEAT A SAMPLE OF THE SUBSTANCE BEFORE THE BLOWPIPE IN A GLASS TUBE SEALED AT ONE END. 24

*a.* NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE: absence of mercury.

*b.* A SUBLIMATE IS FORMED: presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury, which consists of small globules, cannot be confounded with that of cadmium or arsenic.

After the termination of the preliminary examination, proceed to the solution of the substance as directed § 181 (42).

## § 178.

### B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. EVAPORATE A SMALL PORTION OF THE FLUID in a platinum capsule, or in a small porcelain crucible, to ascertain whether it actually contains any matter in solution; if a residue remains, examine this as directed § 176. 25

2. TEST WITH LITMUS-PAPER (blue and red). 26

*a.* THE FLUID REDDENS BLUE LITMUS-PAPER. This reaction may be caused by a free acid or an acid salt, as well as by a metallic salt soluble in water. To distinguish between

these two cases, pour a small quantity of the fluid into a watch-glass, and dip into it a small glass rod, after moistening the extreme point of the latter with dilute solution of carbonate of soda; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt.

*b.* REDDENED LITMUS-PAPER TURNS BLUE: this indicates 27
the presence of a free alkali or an alkaline carbonate, free alkaline earths, alkaline sulphides, and of a number of other salts containing an alkali or, it may be, an alkaline earth, in combination with a weak acid.

3. SMELL THE FLUID, or, should this fail to give satisfactory 28
results, DISTIL, to ascertain whether the simple solvent present is water, alcohol, ether, &c. If you find it is not water, evaporate the solution to dryness, and treat the residue as directed § 176.

4. If the solution is aqueous, and manifests an acid reaction, 29
DILUTE A PORTION OF IT LARGELY WITH WATER. Should this impart a milky appearance to it, the presence of ANTIMONY, or BISMUTH (or possibly also of tin) may be inferred. Comp. § 121, 9, and § 131, 4.

After the termination of the preliminary examination, proceed 30
to the actual examination. If the solution is aqueous, with neutral reaction, it can only contain substances soluble in water; but if it has an acid reaction, arising from the presence of free acid, the actual examination must be conducted with due regard to the possible presence also of bodies soluble in acids, though insoluble in water. Proceed accordingly with neutral aqueous solutions as directed § 182, with acid solutions as directed § 185, if you are quite sure that there is only one acid and one base present; but where there is reason to suppose the presence of several bases and acids, proceed as directed § 189. With fluids of alkaline reaction, proceed as directed § 182, unless there be reason to suppose the presence of more than one acid and one base, when the instructions given in § 189 must be followed.

## II. SOLUTION OF BODIES, OR CLASSIFICATION OF SUBSTANCES, ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOLVENTS.*

### § 179.

Water and acids (hydrochloric acid, nitric acid, aqua regia) are 31
the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective deportment with these solvents.

*First class.*—SUBSTANCES SOLUBLE IN WATER.

*Second class.* — SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

* Consult the remarks in the third section.

*Third class.*—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER AS WELL AS IN HYDROCHLORIC ACID, NITRIC ACID, AND AQUA REGIA.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances (see § 181).

The process of solution is conducted in the following manner.

## A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

### § 180.

1. Put about a gramme of the finely pulverized substance into a small flask or a test-tube, add from ten to twelve times the amount of distilled water, and heat to boiling over a spirit or gas-lamp. 32

*a.* THE SUBSTANCE DISSOLVES COMPLETELY. In that case it belongs to the first class; regard must be had to what has been stated in the preliminary examination (30) with respect to reaction. Treat the solution either as directed § 182, or § 189, according as either one or several acids and bases are supposed to be present. 33

*b.* AN INSOLUBLE RESIDUE REMAINS EVEN AFTER PROTRACTED BOILING. Let the residue subside, and filter the fluid off, if practicable in such a manner as to retain the residue in the test-tube; evaporate a few drops of the clear filtrate on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed 35. But if a residue remains, the substance is at least partly soluble; in which case boil again with water, filter, add the filtrate to the first solution, and treat the fluid, according to circumstances, either as directed § 182, or § 189. Wash the residue with water, and proceed as directed 35. 34

2. Treat a small portion of the residue which has been boiled with water (34) with dilute hydrochloric acid. If it does not dissolve, heat to boiling, and if this fails to effect complete solution, decant the fluid into another test-tube, boil the residue with concentrated hydrochloric acid, and, if it dissolves, add the solution to the fluid in the other test-tube. 35

The reactions which may manifest themselves in this operation, and which ought to be carefully observed, are, ($\alpha$) Effervescence, which indicates the presence of carbonic acid or hydrosulphuric acid; ($\beta$) Evolution of chlorine, which indicates the presence of peroxides, chromates, &c.; ($\gamma$) Emission of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. The analysis of the latter bodies being effected in a somewhat different manner, a special paragraph will be devoted to them (see § 204).

*a.* THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur separates, which may be known by its color and light specific gravity, and may, after boiling some time longer, be removed by filtration; or that gelatinous hydrate of silicic acid separates). 36

Proceed, according as there is reason to suppose the presence of one or of several bases and acids, either as directed § 185, or as directed § 190 after filtration if necessary. The body belongs to the second class. To make quite sure of the actual nature of the sulphur or hydrated silicic acid filtered off, examine these residuary matters as directed § 188, or § 203.

*b.* THERE IS STILL A RESIDUE LEFT. In that case put aside the test-tube containing the specimen which has been boiled with the hydrochloric acid, and try to dissolve another sample of the substance insoluble in water, or already extracted with water, by boiling with nitric acid, and subsequent addition of water. Evolution of nitric oxide, or nitrous acid, by the action of the nitric acid, shows that a process of oxidation is taking place. 37

*α. The sample is completely dissolved, or leaves no other residue but sulphur or gelatinous silicic acid;* in this case also the body belongs to the second class. Use this solution to test further for bases, as directed § 185, or, as the case may be, § 189, III. (**109**), and for the rest proceed as in **36**. 38

*β. There is still a residue left.* Pass on to **40**. 39

3. If the residue insoluble in water will not entirely dissolve in hydrochloric acid nor in nitric acid, try to effect complete solution of it by means of nitro-hydrochloric acid. To this end mix the contents of the tube treated with nitric acid with the contents of the tube treated with concentrated hydrochloric acid; heat the mixture to boiling, and should this fail to effect complete solution, decant the clear fluid off from the undissolved residue, boil the latter for some time with concentrated nitro-hydrochloric acid, and add the decanted solution in dilute aqua regia as well as the solution in dilute hydrochloric acid, decanted in **35**. Heat the entire mixture once more to boiling, and observe whether complete solution has now been effected, or whether the action of the concentrated nitro-hydrochloric acid has still left a residue. In the *latter* case filter the solution—if necessary after addition of some water*—wash the residue with boiling water, and proceed with the filtrate, and the washings added to it, as directed § 185, or § 190. In the *former* case proceed with the clear solution in the same way.† 40

4. If boiling nitro-hydrochloric acid has left an undissolved residue, wash it thoroughly with water, and then proceed as directed § 188, or as directed § 203, according as there is reason to suppose the presence of only one or several bases and acids. 41

* If the fluid turns turbid upon addition of water, this indicates the presence of bismuth or antimony; the turbidity will disappear again upon addition of hydrochloric acid.

† Where the acid solution on cooling deposits acicular crystals, the latter generally consist of chloride of lead; it is in that case often advisable to decant the fluid off the crystals, and to examine the fluid and crystals separately. Where on boiling with aqua regia metastannic chloride has been formed from binoxide of tin, the washing water, dissolving this, becomes turbid on dropping into the strongly acid fluid which has run off first. In that case receive the washing water in a separate vessel, and treat the two solutions separately with hydrosulphuric acid as directed in § 190, but filter afterwards through the same filter.

## B. The Substance under Examination is a Metal or an Alloy.

### § 181.

The metals are best classed according to their behaviour with nitric acid, as follows: 42

I. Metals which are not attacked by nitric acid: gold, platinum.

II. Metals which are oxidized by nitric acid, but whose oxides do not dissolve in an excess of the acid or in water: antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates which dissolve in an excess of the acid or in water: all the other metals.

Pour nitric acid of 1·20 sp. gr. over a small portion of the substance, and apply heat.

1. Complete solution takes place, either at once or upon addition of water; this proves the absence of platinum,* gold, antimony,† and tin. Proceed either as directed § 182, or § 189, III. (109), according as there is reason to suppose the presence of only one or of several metals. 43

2. A residue is left.

*a. A metallic residue.* Filter, and treat the filtrate as directed § 189, III. (109), after having seen, in the first place, whether anything has really been dissolved. Wash the residue thoroughly, dissolve in nitro-hydrochloric acid, and test the solution for gold and platinum, according to § 128. 44

*b. A white pulverulent residue;* indicates antimony and tin. Filter, ascertain whether anything has been dissolved, then treat the filtrate as directed § 189, III. (109). Wash the residue thoroughly, then test for teroxide of antimony, binoxide of tin, and arsenic acid, according to § 134, 5. (Part, at least, of the arsenic acid is always found in this precipitate, combined with teroxide of antimony and binoxide of tin.) 45

* Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

† Very minute traces of antimony, however, are often completely dissolved by nitric acid.

## III. Actual Examination.

### *Simple Compounds.**

### A Substances soluble in Water.

### *Detection of the Base.*†

§ 182.

1. Add some hydrochloric acid to a portion of the aqueous solution. 46

*a.* No precipitate is formed; indicates the absence of silver and suboxide of mercury, and likewise the absence of considerable quantities of lead. Pass on to 50.

*b.* A precipitate is formed. Divide the fluid in which the precipitate is suspended into two portions, and add ammonia in excess to the one. 47

*a. The precipitate redissolves, and the fluid becomes clear:* this shows the precipitate to have consisted of chloride of silver, and is consequently indicative of the presence of silver. To arrive at a positive conviction on this point, the original solution must be tested with chromate of potassa, and with hydrosulphuric acid (see § 115, 4, and § 138, 7).

*β. The precipitate turns black:* this shows the precipitate to have consisted of subchloride of mercury, which has now been converted by the ammonia into the black compound; it is consequently indicative of the presence of suboxide of mercury. To set all doubt at rest, test the original solution with protochloride of tin, and with metallic copper (see § 116). 48

*γ. The precipitate remains unaltered;* it consists of chloride of lead, which is not dissolved by ammonia; this reaction is accordingly indicative of the presence of lead. Whether the precipitate consists really of chloride of lead or not is conclusively ascertained: 1st, by diluting the second portion of the fluid in which the precipitate produced by hydrochloric acid is suspended, with a large amount of water, and applying heat; the precipitate must dissolve if it consists of chloride of lead; and 2nd, by testing portions of the original solution with hydrosulphuric acid and sulphuric acid (§ 117, 4, and 8). 49

2. Add to the fluid acidified with hydrochloric acid solution of hydrosulphuric acid until it smells distinctly of that gas after shaking, heat the mixture, add some more solution of hydrosulphuric acid, and let it stand a short time.‡ 50

* This term is used to designate compounds supposed to contain only *one* base and *one* acid, or *one* metal and *one* non-metallic element. The principal object of this chapter is to facilitate instruction in analysis, as it is advantageous that the examination of complex compounds should be preceded by the analysis of simple compounds. In actual practical analyses, use can be made of this chapter only exceptionally, as there exists no outward sign by which to judge whether a substance contains only one base or acid, or several.

† Arsenious and arsenic acids, and silicic acid, are included here.

‡ If a precipitate forms immediately upon addition of solution of hydrosulphuric

*a.* THE FLUID REMAINS CLEAR. Pass on to **56**, since this is a proof that lead, bismuth, copper, cadmium, oxide of mercury, gold, platinum, tin, antimony, arsenic, and sesquioxide of iron are not present.

*b.* A PRECIPITATE IS FORMED.

*a.* THE PRECIPITATE IS WHITE; it consists of separated sulphur, and indicates a substance which decomposes hydrosulphuric acid.* Of the metallic oxides which possess this property SESQUIOXIDE OF IRON is the most common (§ 111, 3). Test for this with ammonia and ferrocyanide of potassium in the original solution (§ 111, 5 and 6). If it is not found, pass on to **56**. **51**

*β.* THE PRECIPITATE IS YELLOW; it may consist of sulphide of cadmium, sulphide of arsenic, or bisulphide of tin; it indicates accordingly cadmium, arsenic, or binoxide of tin. To distinguish between them, mix a portion of the fluid wherein the precipitate is suspended with ammonia in excess, add some sulphide of ammonium, and warm. **52**

*aa. The precipitate does not dissolve*: it consists of CADMIUM; for sulphide of cadmium is insoluble in ammonia and sulphide of ammonium. Confirm by testing the original substance, or the precipitate thrown down from the original solution by carbonate of ammonia, with the blowpipe (§ 122, 9).

*bb. The precipitate dissolves:* BINOXIDE OF TIN or ARSENIC: add ammonia to a small portion of the original solution.

*aa. A white precipitate is formed.* BINOXIDE OF TIN is the substance present. Confirm by reducing the precipitate before the blowpipe, with cyanide of potassium and carbonate of soda (§ 130, 8).

*ββ. No precipitate is formed.* This indicates ARSENIC. Confirm by the production of an arsenical mirror from the original substance or the precipitated sulphide of arsenic, either with cyanide of potassium and carbonate of soda, or in some other way; and moreover by exposing the original substance with carbonate of soda to the inner flame of the blowpipe (§ 132, 12 and 13). If the solution contained arsenious acid, the yellow precipitate formed immediately upon the addition of the hydrosulphuric acid; if arsenic acid, it formed only upon the application of heat, or after long standing. For further information respecting the means of distinguishing between the two acids see § 134, 9.

*γ.* THE PRECIPITATE IS ORANGE-COLORED, it consists of tersulphide of antimony, and indicates TEROXIDE OF ANTIMONY. For confirmation the original solution is tested with zinc in a platinum capsule (§ 131, 8). **53**

*δ.* THE PRECIPITATE IS DARK-BROWN. It consists of protosulphide of tin, and indicates PROTOXIDE OF TIN. To **54**

acid, it is unnecessary to apply heat, &c.; but if the fluid remains clear, or is rendered only slightly turbid, the above course of proceeding must be strictly followed, to guard against the risk of overlooking arsenic acid and binoxide of tin.

* If the colour of the solution from being reddish yellow changes to green, chromic acid is indicated.

confirm, test a portion of the original solution with chloride of mercury (§ 129, 8).

*ε.* THE PRECIPITATE IS BROWNISH-BLACK OR BLACK. It 5
may consist of sulphide of lead, sulphide of copper, tersulphide of bismuth, tersulphide of gold, bisulphide of platinum, or sulphide of mercury. To distinguish between these different sulphides, the following experiments with the original solution are resorted to,

*aa.* Add dilute sulphuric acid to a portion; a white precipitate indicates LEAD. To confirm, test with chromate of potassa (§ 117, 9).

*bb.* Add solution of soda to a portion; a yellow precipitate indicates OXIDE OF MERCURY. Confirm with protochloride of tin and copper (§ 119).

The presence of oxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the solution of hydrosulphuric acid in the fluid under examination is observed to pass; this precipitate is white at first, but changes upon the addition of more of the precipitant to yellow, then to orange, and finally to black (§ 119, 3). With *very acid* solutions the reaction with potassa or soda is not effective (§ 119, 4).

*cc.* Add ammonia in excess to a portion; if a bluish precipitate is formed which redissolves in an excess of the precipitant to an azure color, or even if the ammonia simply colors the solution azure-blue, this indicates COPPER. To confirm, test with ferrocyanide of potassium (§ 120, 9).

*dd.* If the precipitate produced by ammonia was white, and excess of ammonia has failed to redissolve it, filter the fluid off, wash the precipitate, dissolve a portion of it on a watch-glass in 1 or 2 drops of hydrochloric acid, with addition of 2 drops of water, and then add more water. If the solution turns milky, this is caused by basic terchloride of bismuth: the reaction consequently indicates BISMUTH. Confirm by testing the remaining portion of the ammonia precipitate with a solution of protochloride of tin in soda (§ 121, 10).

*ee.* Add solution of sulphate of protoxide of iron to a portion. A fine black precipitate indicates GOLD. To confirm, expose the precipitate to the flame of the blowpipe, or test the original solution with protochloride of tin (§ 126).

*ff.* Add chloride of potassium and alcohol to a portion; a yellow crystalline precipitate indicates PLATINUM. To confirm, heat the precipitate to redness (§ 127).

3. Mix a small portion of the original solution with chloride of 56
ammonium,* add ammonia to alkaline reaction, and then no matter whether the latter reagent has produced a precipitate or not, a little sulphide of ammonium, and warm, if a precipitate fails to separate in the cold.

* The chloride of ammonium is used for the purpose of preventing the precipitation by ammonia of any magnesia which might be present.

*a.* NO PRECIPITATE IS FORMED; pass on to **62**; for iron, cobalt, nickel, manganese, zinc, chromium, alumina, and silicic acid, are not present.*

*b.* A PRECIPITATE IS FORMED.

*a.* *The precipitate is black;* protoxide of iron,† nickel, or **57**
cobalt. Mix a portion of the original solution with some potassa or soda.

*aa.* A dirty greenish-white precipitate is formed, which soon changes to a reddish-brown upon exposure to the air; PROTOXIDE OF IRON. Confirm with ferricyanide of potassium (§ 110).

*bb.* A precipitate of a light greenish tint is produced, which does not change color: NICKEL. Confirm with ammonia, and addition of potassa or soda (§ 108).

*cc.* A sky-blue precipitate is formed, which turns to a light-red upon boiling, or is discolored and acquires a dark tint: COBALT. Confirm by the blowpipe (§ 109).

*β.* *The precipitate is not black.* **58**

*aa.* If the precipitate is distinctly flesh-colored it consists of sulphide of manganese, and is consequently indicative of PROTOXIDE OF MANGANESE. To confirm, add soda to the original solution, or test before the blowpipe (§ 107).

*bb.* If the precipitate is bluish-green, it consists of hydrated sesquioxide of chromium, and is consequently indicative of SESQUIOXIDE OF CHROMIUM. To confirm, test the original solution with soda, before the blowpipe (§ 102).

*cc.* If the precipitate is white, and does not dissolve on **59**
warming with more sulphide of ammonium,‡ it may consist of hydrate of alumina, hydrate of silicic acid, or sulphide of zinc, and may accordingly point to alumina, oxide of zinc or silicic acid; the latter, in that case, is generally contained in the original solution as an alkaline silicate. To distinguish between these three bodies, add soda cautiously to a portion of the original solution, and wait to see whether this produces a precipitate; then add more soda until the precipitate formed is re-dissolved.

*aa.* If solution of soda fails to produce a precipitate, **60**
there is reason to test for SILICIC ACID. For that purpose evaporate a portion of the original solution with excess of hydrochloric acid to dryness, and treat the residue with hydrochloric acid and water (§ 150, 2), when the silicic acid will be left undissolved. Determine the nature of the alkali which has been dissolved as directed **65**.

*ββ.* If soda produces a precipitate, which re-dissolves in

* With regard to alumina and many of these metals, the above conclusion does not hold good in the presence of organic matter, especially of non-volatile organic acids. In this case and if the preliminary examination pointed to one of the metals of the third or fourth group, fuse a portion of the original substance with carbonate and nitrate of soda, soak the fusion in water, add hydrochloric acid, heat, filter, and test the solution so obtained according to 56.

† Sesquioxide of iron would have been found already in 51.

‡ A white precipitate produced by sulphide of ammonium and soluble in excess on warming would consist of sulphur. And sulphur might be separated here by such a body as a ferricyanide.

excess, add to a portion of this alkaline fluid *a little* sulphuretted hydrogen water (*i. e.*, so that a considerable excess of the soda may remain unchanged). A white precipitate indicates ZINC. Confirm by cobalt solution before the blowpipe (§ 106). If sulphuretted hydrogen produces no precipitate, add chloride of ammonium to the rest of the alkaline fluid and heat. A white precipitate insoluble in excess of chloride of ammonium indicates ALUMINA. Confirm by cobalt solution before the blowpipe (§ 101).

*Note to* **58** *and* **59.**

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered in **58** and **59**, it is advisable, in all cases where the least impurity is suspected, to adopt the following method for the detection of manganese, chromium, zinc, alumina, and silicic acid.

Add solution of soda to a portion of the original solution, first in small quantity, then in excess.

*aa. No precipitate is formed:* SILICIC ACID may be assumed to be present; proceed as directed **60**. **61**

*bb. A whitish precipitate is formed*, which does not redissolve in an excess of the precipitant, and speedily turns blackish-brown upon exposure to the air: MANGANESE. Confirm by the blowpipe (§ 107).

*cc. A precipitate is formed*, which redissolves in an excess of the precipitant: SESQUIOXIDE OF CHROMIUM, ALUMINA, OXIDE OF ZINC.

*αα.* To a portion of the alkaline solution add *a little* hydrosulphuric acid water (*i. e.*, so that a considerable excess of the soda may remain unchanged). A white precipitate indicates ZINC.

*ββ.* If the original solution is green or violet, or the alkaline solution is green, and if the precipitate produced by soda and redissolved by excess was of a bluish color, SESQUIOXIDE OF CHROMIUM is present. To confirm, heat the alkaline solution to boiling or try the reaction before the blowpipe (§ 102).

*γγ.* Add chloride of ammonium to the alkaline solution and heat. A white precipitate insoluble in excess of chloride of ammonium indicates ALUMINA. Confirm by cobalt solution before the blowpipe (§ 101).

4. Add to a portion of the original solution chloride of ammonium and carbonate of ammonia, mixed with some ammonia, and heat gently. **62**

*a.* NO PRECIPITATE IS FORMED: absence of baryta, strontia, and lime. Pass on to **64**.

*b.* A PRECIPITATE IS FORMED: presence of baryta, strontia, or lime. Filter off the precipitate, wash it, dissolve it in dilute hydrochloric acid, evaporate the solution to dryness, warm the residue with water, filter and add to a portion of this solution a large quantity of solution of sulphate of lime. **63**

*a. The solution does not become turbid, even after the lapse of*

*five or ten minutes:* LIME. Confirm with oxalate of ammonia (§ 97)

*β. The solution becomes turbid, but only after the lapse of some time:* STRONTIA. Confirm by the flame-coloration (§ 96, 7 or 8).

*γ. A precipitate is immediately formed:* BARYTA. Confirm with hydrofluosilicic acid (§ 95).

5. Mix that portion of the solution in which carbonate of ammonia has, after previous addition of chloride of ammonium, failed to produce a precipitate (62), with phosphate of soda, add more ammonia, and rub the sides of the vessel with a glass rod gently. 64

*a.* NO PRECIPITATE IS FORMED: absence of magnesia. Pass on to 65.

*b.* A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. Evaporate a drop of the original solution on perfectly clean platinum-foil as slowly as possible, and gently ignite the residue. 65

*a.* THERE IS NO FIXED RESIDUE LEFT. Test for AMMONIA, by adding to the original solution hydrate of lime, and observing the odor and reaction of the escaping gas, and the fumes which it forms with acetic acid (§ 91).

*b.* THERE IS A FIXED RESIDUE LEFT: potassa or soda. 66 Add bichloride of platinum to a portion of the original solution (having first evaporated it to a very small bulk if dilute), and shake the mixture or rub with a glass rod.

*α. No precipitate is formed, not even after ten or fifteen minutes:* SODA. Confirm with the flame coloration or with antimonate of potassa (§ 90).

*β. A yellow crystalline precipitate is formed:* POTASSA. Confirm with tartaric acid or the flame coloration (§ 89).

*Simple Compounds.*

## A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

### I. *Detection of Inorganic Acids.*

### § 183.

Reflect in the first place which of the inorganic acids form soluble compounds with the detected base (compare Appendix IV.) and bear this in mind in your subsequent operations, giving due regard also to the results of the preliminary examination.

1. ARSENIOUS ACID and ARSENIC ACID have already been found in the detection of the base. They are distinguished from each other by their reaction with nitrate of silver, or with potassa and sulphate of copper (see § 134, 9). 67

2. The presence of CARBONIC ACID in combination with bases, SULPHUR in combination with metals, and CHROMIC ACID, has been also indicated already in the detection of the base. The two former betray their presence by effervescing upon the addition of hydrochloric acid; the escaping gases may be distinguished from one another by the smell. The presence of carbonic acid may be con- 68

firmed by lime water (see § 149), and that of hydrosulphuric acid by acetate of lead (§ 156). Free carbonic acid and free hydrosulphuric acid in aqueous solution may be detected by the same reagents. The presence of chromic acid is invariably indicated by the yellow or red tint of the solution, as well as by the transition of the red or yellow colour to green, and the separation of sulphur, upon the addition of hydrosulphuric acid water. Confirm with acetate of lead and nitrate of silver (§ 138).

3. Acidify a portion of the solution with hydrochloric acid, or —if oxide of silver or suboxide of mercury has been found—with nitric acid, and add chloride of barium or nitrate of baryta as the case may be. Should a gelatinous precipitate of silicic acid form on addition of hydrochloric acid, repeat the experiment after having diluted the fluid considerably. In this case it is also best to add the acid all at once and not gradually, compare § 150, 2. 69

*a.* THE FLUID REMAINS CLEAR. Absence of sulphuric acid. Pass on to **70.**

*b.* A PRECIPITATE IS PRODUCED, IN FORM OF A FINE WHITE POWDER: SULPHURIC ACID. The precipitate must remain undissolved even after further addition of dilute hydrochloric or nitric acid.

4. Add solution of sulphate of lime to another portion of the solution (which, if it has an acid reaction, must first be neutralized, or made slightly alkaline, by ammonia, and if necessary, filtered). 70

*a.* NO PRECIPITATE IS FORMED: absence of phosphoric acid, silicic acid, oxalic acid, and fluorine. Pass on to **73.**

*b.* A PRECIPITATE IS FORMED. Add acetic acid in excess. 71

*α. The precipitate redissolves readily:* PHOSPHORIC ACID or SILICIC ACID. Evaporate a portion of the original solution, after acidifying with hydrochloric acid, to dryness, and treat the residue with some hydrochloric acid and water. If an insoluble residue is left, it consists of SILICIC ACID. If no residue remains, mix a sample of the original solution with chloride of ammonium, sulphate of magnesia, and ammonia. A crystalline precipitate shows the presence of PHOSPHORIC ACID (§ 142).

*β. The precipitate remains undissolved or dissolves with difficulty:* OXALIC ACID or FLUORINE. Oxalate of lime is pulverulent, fluoride of calcium flocculent and gelatinous. If oxalic acid is suspected, confirm by treating the original substance with binoxide of manganese and sulphuric acid (§ 145). If fluorine is suspected, confirm by applying the etching test to the original substance (§ 146). 72

5. Acidify a fresh portion of the solution with nitric acid, and add solution of nitrate of silver. 73

*a.* THE FLUID REMAINS CLEAR. This is a proof of the absence of chlorine, bromine, iodine, ferrocyanogen, and ferricyanogen; the absence of cyanogen (in simple cyanides) is also probable. (Of the soluble cyanides, cyanide of mercury is not precipitated by nitrate of silver; if, therefore, in detection of the base mercury has been found, cyanide of mercury may be present. For the manner of detecting the cyanogen in the latter see § 155, 11.) Pass on to **76.**

*b.* A PRECIPITATE IS FORMED.

*α. The precipitate is orange:* FERRICYANOGEN. Confirm 74 with sulphate of iron (§ 155, Appendix).

*β. The precipitate is white or yellowish-white.* Treat the precipitate with ammonia in excess—immediately, if the base was an alkali or an alkaline earth—after filtering and washing, if the base was an earth or the oxide of a heavy metal.

*αα.* The precipitate is not dissolved: IODINE or FERROCYANOGEN. In the former case the precipitate is pale yellow, in the latter white and gelatinous. Confirm for iodine with starch and hyponitric acid (§ 154), for ferrocyanogen with sesquichloride of iron (§ 155, Appendix).

*ββ.* The precipitate is dissolved: CHLORINE, BROMINE, 75 or CYANOGEN. If the original substance smells of hydrocyanic acid, and the silver precipitate dissolves with some difficulty in ammonia, CYANOGEN is indicated. Confirm by adding to the original solution sulphate of iron, soda, and then hydrochloric acid (§ 155). If addition of chlorine-water imparts a yellow tint to the original solution, BROMINE is indicated; if the bromine is present only in small proportion, chloroform or bisulphide of carbon must be used in conjunction with the chlorine-water (§ 153). In the proved absence of both bromine and cyanogen the precipitate shows the presence of CHLORINE.

6. Add to a small portion of the aqueous solution hydrochloric 76 acid, drop by drop, until a distinct acid reaction is just imparted to the fluid, then dip in a slip of turmeric-paper, take it out and dry it at 100°. If the dipped portion looks brownish-red, BORACIC ACID is present. Confirm by adding sulphuric acid and alcohol, and setting fire to the latter (§ 144).

7. With regard to NITRIC ACID and CHLORIC ACID, these are 77 usually discovered in the preliminary examination (6). Confirm for the former with sulphate of iron and sulphuric acid (§ 159); for the latter by treating the solid salt with concentrated sulphuric acid, (§ 160).

*Simple Compounds.*

## A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

### II. *Detection of Organic Acids.*

### § 184.

Consider, in the first place, which of the organic acids form soluble compounds with the detected base (compare Appendix IV.), and bear this in mind in your subsequent operations, giving due regard also to the results of the preliminary examination.

The following course presupposes the organic acid to be present in the free state, or in combination with an alkali or an alkaline earth. If the detected base belongs to another group, therefore, it must first be removed. Where the base belongs to group V. or group

VI. the removal is effected by hydrosulphuric acid, where it belongs to group IV. by sulphide of ammonium. After filtering off the sulphides, and removing the excess of sulphide of ammonium by acidifying with hydrochloric acid, heating, and filtering off the sulphur, proceed to **78**. Where the base is alumina or sesquioxide of chromium, try first to precipitate these substances by boiling with carbonate of soda; should this fail, as it will where the acid is non-volatile, precipitate the latter in a fresh portion of the solution with neutral acetate of lead, wash the precipitate, diffuse it through water, pass hydrosulphuric acid, filter off the sulphide of lead and treat the filtrate as directed below. Alumina may also be precipitated from its compounds with non-volatile organic acids by solution of soluble glass, as silicate of alumina. To separate acetic or formic acid from bases which lie in the way of their detection, you may also distil the salt with dilute sulphuric acid.

1. Add ammonia to a portion of the aqueous solution to slight alkaline reaction, then chloride of calcium in sufficient quantity. If the solution was neutral, or only slightly acid, add chloride of ammonium before adding the chloride of calcium. **78**

*a.* NO PRECIPITATE IS FORMED, EVEN AFTER SHAKING THE FLUID AND AFTER THE LAPSE OF A FEW MINUTES: absence of oxalic acid and tartaric acid. Pass on to **80**.

*b.* A PRECIPITATE IS FORMED. **79**

*a. The precipitate takes some time to form and is crystalline:* TARTARIC ACID. Confirm by testing the behaviour of the washed precipitate with soda or with ammonia and nitrate of silver, or by testing the aqueous solution with acetate of potassa and acetic acid (§ 163).

*β. The precipitate forms immediately and is finely pulverulent:* OXALIC ACID. Confirm by acidifying a fresh portion of the aqueous solution with acetic acid and adding solution of sulphate of lime (§ 145).

2. Heat the fluid of 1, *a*, to boiling, keep at that temperature for some time, and add some more ammonia to the boiling fluid. **80**

*a.* IT REMAINS CLEAR: absence of citric acid. Pass on to **81**.

*b.* IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID.* Confirm by preparing the lead salt, washing it, and testing its deportment with ammonia, in which it readily dissolves; or preferably by preparing the characteristic baryta salt and examining it with the microscope (§ 164).

3. Mix the fluid of 2, *a*, with 2 volumes of alcohol. **81**

*a.* IT REMAINS CLEAR even after long standing: absence of malic and succinic acids. Pass on to **82**.

*b.* A PRECIPITATE is formed: MALIC or SUCCINIC ACID. Heat a portion of the original solid substance with nitric acid, evaporate to dryness altogether, boil the residue with solution of carbonate of soda, filter if necessary, neutralize *exactly* with hydrochloric acid and test one portion of this solution with

* If the ammonia contains carbonic acid, a precipitate of carbonate of lime may form here. Such a precipitate may be readily distinguished from citrate of lime by hydrochloric acid.

sulphate of lime; another portion with sesquichloride of iron. A precipitation (of oxalate of lime) by the former indicates malic acid;* a precipitation by the latter indicates succinic acid. For further confirmation prepare the lead salt of the acid and examine its properties, compare § 165, 5 and § 168, 5.

4. Neutralize a portion of the original solution *completely* (if not already absolutely neutral) with ammonia or hydrochloric acid, and add sesquichloride of iron. 82

*a.* A REDDISH YELLOW BULKY PRECIPITATE FORMS: BENZOIC ACID. Confirm by treating the original dry substance with hydrochloric acid (§ 169, 2).

*b.* THE LIQUID ACQUIRES A RATHER INTENSE DEEP RED TINT, AND, UPON BOILING, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. If the original substance is a solid, warm a portion with sulphuric acid and alcohol (§ 171). If the original substance is a fluid, having neutralized a portion with soda in case it is acid, evaporate it to dryness, and test the residue. The odor of acetic ether indicates ACETIC ACID. 83

If you do not detect acetic acid, you may conclude that the substance contains FORMIC ACID: confirm with nitrate of silver and chloride of mercury (§ 172).

## *Simple Compounds.*

### B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

*Detection of the Base.*†

§ 185.

Dilute a portion of the solution in hydrochloric acid, nitric acid, or nitro-hydrochloric acid with water,‡ and proceed to examine for bases of the *second, fifth,* and *sixth groups* according to § 182, beginning at 46 if the solvent was nitric acid, at 50 if the solvent contained hydrochloric acid. It is to be noted here that hydrochloric acid when used as a solvent does not usually alter the state of oxidation of the base present, while nitric acid and nitro-hydrochloric acid generally have the effect of more or less oxidizing the base where this is possible. Hence when oxide of mercury, binoxide of tin, or sesquioxide of iron is found, and nitric or nitro-hydrochloric acid has been used for dissolving, you must examine the original substance specially to see in what state the metal is actually present, if this is not at once evident from the solubility. In the case of mercury salts for instance, treatment with soda would decide which 84

* Compare end of § 165, 1.

† Regard is also had here to certain salts of the alkaline earths, as this course of examination leads directly to their detection.

‡ If upon the addition of water the liquid becomes white and turbid or deposits a white precipitate, this indicates antimony or bismuth (possibly also tin). Compare § 121, 9, and § 131, 4. Heat with hydrochloric acid until the fluid has become clear again, then pass to 50.

of the oxides were present, for this reagent separates yellow oxide from the salts of the oxide, and black suboxide from the salts of the suboxide.

In testing for bases of the *third* and *fourth groups*, with sulphide of ammonium, according to **56**, the usual course is departed from. We have seen (**59**), that if in cases where we have A SUBSTANCE SOLUBLE IN WATER we obtain a white precipitate upon adding chloride of ammonium, ammonia, and sulphide of ammonium, this precipitate can consist only of SULPHIDE OF ZINC, ALUMINA, HYDRATE OF SILICIC ACID, or SULPHUR. But the case is different if the body is INSOLUBLE IN WATER, but dissolves in hydrochloric acid; for in that case a white precipitate produced by ammonia, in presence of chloride of ammonium, may consist also of PHOSPHATES, BORATES, OXALATES, SILICATES OF THE ALKALINE EARTHS, or FLUORIDES OF THEIR METALS, since all these bodies are insoluble in water, but dissolve in hydrochloric acid, and (being only sparingly soluble in chloride of ammonium) separate again upon neutralization of that acid. In the presence of organic substances, this precipitate may also proceed from compounds of TARTARIC ACID and CITRIC ACID with several ALKALINE EARTHS.

If, therefore, a white precipitate is produced upon testing an acid solution, under the circumstances stated, and in pursuing the course laid down in § 182 (**56**), proceed as follows:—

1. If the results of the preliminary examination have given you **85** reason to suspect SILICIC ACID (**20**), evaporate a portion of the hydrochloric acid solution to dryness, moisten the residue with hydrochloric acid and add water. If silicic acid is present, it will remain undissolved. Determine the base in the solution as directed **56** or **62**, as the case may be.

2. Add to a portion of the original hydrochloric acid solution **86** some tartaric acid, and after this ammonia in excess.

*a.* NO PERMANENT PRECIPITATE IS FORMED: absence of the above enumerated salts of the alkaline earths. Mix another portion of the original solution with soda in excess, and add to the one half of the clear fluid chloride of ammonium, to the other half a small quantity of solution of hydrosulphuric acid. The formation of a precipitate in the former (insoluble in excess of the reagent) indicates ALUMINA; in the latter, ZINC.

*b.* A PERMANENT PRECIPITATE IS FORMED: presence of a salt of an alkaline earth.

*α.* Bring a sample of the original substance, on a watch- **87** glass, in contact with a few drops of water, and some concentrated sulphuric acid, and then add some binoxide of manganese free from carbonates. If evolution of carbonic acid takes place instantly, the salt is an OXALATE. To find the base, ignite a fresh sample, dissolve the residue in dilute hydrochloric acid, and examine the solution as directed **62**.

*β.* Add to a portion of the hydrochloric acid solution am- **88** monia until a precipitate forms; then acetic acid until this is redissolved; lastly, acetate of soda, and a drop of sesquichloride of iron: the formation of a white flocculent precipitate indicates PHOSPHORIC ACID. Add now some more

sesquichloride of iron until the fluid has acquired a distinct red color, boil, filter boiling, and (after having removed, by ammonia, the iron which may have been dissolved) test the filtrate, now free from phosphoric acid, for the alkaline earth with which the phosphoric acid was combined, as directed 62.

γ. BORACIC ACID is detected in the weak hydrochloric acid 89 solution by turmeric-paper (§ 144), and the base combined with it, by boiling a portion of the original substance with water and carbonate of soda, filtering, washing, dissolving the carbonate formed in the least possible amount of dilute hydrochloric acid, evaporating the solution to dryness, treating the residue with water, filtering if required, and testing according to 62.

δ. Test for FLUORINE, by heating a portion of the original substance, or of the precipitate produced in the hydrochloric acid solution by ammonia, with sulphuric acid (§ 146). After removal of the fluorine, ascertain the nature of the alkaline earth which you have now in the residue, in combination with sulphuric acid.

ε. TARTARIC ACID or CITRIC ACID could only be present if the substance carbonized when ignited in the glass tube. The base is in that case found according to 87 and the acid according to § 187.

*Simple Compounds.*

## B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO HYDROCHLORIC ACID.

*Detection of the Acid.*

### I. *Detection of Inorganic Acids.*

### § 186.

1. CHLORIC ACID cannot be present, since all chlorates are 90 soluble in water; NITRIC ACID, which may be present in form of a basic salt, must have been revealed already by the ignition of the substance in a glass tube, and so must CYANOGEN (8). For the analysis of the CYANIDES insoluble in water see § 204. The results of the test with phosphate of soda and ammonia will have directed attention to the presence of SILICIC ACID. Evaporation of the hydrochloric acid solution to dryness, and treatment of the residue with hydrochloric acid and water, will remove all doubt on this point.

2. ARSENIOUS and ARSENIC ACID,* CARBONIC ACID, CHRO- 91 MIC ACID and SULPHUR in the form of metallic sulphides, would have been already detected in the preliminary examination, in the process of solution, or in the examination for the base. Chromic acid would have been indicated by the yellow or red color of the substance, by the evolution of chlorine on boiling with hydro-

* Hydrosulphuric acid is the best reagent to distinguish between arsenious and arsenic acid in compounds insoluble in water but soluble in hydrochloric acid, § 134, 9.

ch oric acid and by the subsequent detection of sesquioxide of chromium in the solution. Its presence is confirmed by fusing with carbonate of soda (§ 138).

3. Boil a portion of the substance with nitric acid. **92**

*a.* If nitric oxide is evolved, and sulphur separates, this is confirmative of the presence of a metallic SULPHIDE.

*b.* If violet vapours escape, the compound is a metallic IODIDE.*

*c.* If reddish-brown fumes of a chlorine-like smell are evolved, the compound is a metallic BROMIDE,* in which case the fumes will color starch yellow (§ 153).

4. Dilute a small portion of the nitric acid solution—or of the **93** filtrate of this solution, should the nitric acid have left an undissolved residue—and add nitrate of silver. A white precipitate, which, after washing, is soluble in ammonia, and fuses without decomposition when heated, indicates CHLORINE.*

5. Boil a portion of the substance with hydrochloric acid, filter **94** if necessary, dilute with water, and add chloride of barium. A white precipitate, which does not redissolve even upon addition of a large quantity of water, indicates SULPHURIC ACID.

6. Test for BORACIC ACID as directed § 144, 6. **95**

7. If none of the acids enumerated from 1 to 6 are present, there is reason to suspect the presence of PHOSPHORIC ACID, OXALIC ACID, or FLUORINE, or the total absence of acids. To the presence of oxalic acid your attention will have been called already in the course of the preliminary examination (8). Phosphoric acid and fluorine have been found already if they were combined with an alkaline earth, and also oxalic acid, if combined with baryta, strontia, or lime, **87** to **89**; they need therefore here be tested for only where the examination has revealed the presence of some other base. To that end precipitate the base, if belonging to Group V. or VI., with hydrosulphuric acid, or if belonging to Group IV., with sulphide of ammonium, and filter. If you have precipitated with sulphide of ammonium, add to the filtrate hydrochloric acid to acid reaction, expel in either case the hydrosulphuric acid by boiling, and filter if necessary. Test a portion of this solution for phosphoric acid, oxalic acid, and fluorine, as directed **70**. If the base was alumina or sesquioxide of chromium or magnesia, test for phosphoric acid with molybdate of ammonia in the nitric acid solution of the substance (§ 142, 10); for oxalic acid with binoxide of manganese and sulphuric acid (§ 145); for fluorine with sulphuric acid (§ 146).

* It is sometimes more convenient, as for instance in the case of subiodide, subbromide and subchloride of mercury, to test for the halogen by boiling the substance with soda, filtering, and testing the filtrate according to 73.

*Simple Compounds.*

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN ACIDS.

*Detection of the Acid.*

II. *Detection of Organic Acids.*

§ 187.

1. FORMIC ACID cannot be present, as all the formates are 96
soluble in water.

2. ACETIC ACID has been revealed already in the preliminary examination, by the evolution of acetone. Confirm with sulphuric acid and alcohol (§ 171).

3. BENZOIC ACID is usually detected by its separating on solution of the substance in hydrochloric acid, or when the hydrochloric solution cools. Confirm by washing and drying the precipitate and then subliming it.

4. Boil a portion of the substance for some time with solution of 97
carbonate of soda in excess, and filter hot. You have now, in most cases, the organic acid in solution in combination with soda. Acidulate the solution slightly with hydrochloric acid, expel the carbonic acid by heat, and test as directed § 184. With bases of the fourth group and also in presence of oxide of lead, this mode of separation is not completely successful. In exceptional cases of the kind add to the filtrate, after boiling with carbonate of soda, sulphide of ammonium until the whole of the metallic oxide is thrown down, filter and proceed as above.

*Simple Compounds.*

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND NITRO-HYDROCHLORIC ACID.

*Detection of the Base and the Acid.*

§ 188.

Under this head we have to consider the following substances as 98
the only bodies likely to be met with, viz.—SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, FLUORIDE OF CALCIUM, SILICA, strongly ignited or native ALUMINA, SULPHATE OF LEAD, compounds of LEAD with CHLORINE and BROMINE; compounds of SILVER with CHLORINE, BROMINE, IODINE, and CYANOGEN; ignited or native BINOXIDE OF TIN, ignited SESQUIOXIDE OF CHROMIUM, and lastly SULPHUR and CARBON. For the simple silicates I refer to § 205, for the ferro- and ferricyanides to § 204. Whether or no these latter compounds are to be suspected, you will have learnt from the preliminary examination.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are so sparingly soluble that complete solution of them is seldom effected, they are included here also to ensure their detection, should they have been overlooked in the examination of the aqueous or acid solution.

1. Free SULPHUR must have been detected already in the preliminary examination.

2. CARBON is generally black; it is insoluble in aqua regia; put on platinum foil, with the blowpipe flame playing upon the under side of the foil, it is consumed;* by deflagration with nitrate of potassa it yields carbonate of potassa.

3. SESQUIOXIDE OF CHROMIUM is green or blackish green and would have been previously detected in the microcosmic bead (18).

4. Pour sulphide of ammonium over a very small quantity of the substance. 99

*a.* IT TURNS BLACK; this indicates a salt of lead or silver.

*a. The body fused in the glass tube without decomposition* (3): chloride of lead, bromide of lead; chloride of silver, bromide of silver, iodide of silver. Fuse one part of the compound with 4 parts of carbonate of soda and potassa in a small porcelain crucible, let cool, boil the residue with water, and test the filtrate for CHLORINE, BROMINE, and IODINE, as directed 73. Dissolve the residue, which consists either of metallic SILVER or OXIDE OF LEAD, in nitric acid, and test the solution as directed 46.

*β. The body evolved cyanogen by ignition in the glass tube, and left metallic silver behind:* CYANIDE OF SILVER.

*γ. The body remained unaltered by ignition in the glass tube:* SULPHATE OF LEAD. Boil a sample of it with solution of carbonate of soda, filter, acidulate the filtrate with hydrochloric acid and test with chloride of barium for SULPHURIC ACID; dissolve the washed residue in nitric acid, and test the solution with hydrosulphuric acid and with sulphuric acid for LEAD.

*b.* IT REMAINS WHITE: absence of a salt of lead or silver. 100

*a.* Test a portion for BINOXIDE OF TIN with a borax bead colored slightly blue with oxide of copper (§ 129, 12). If a reddish brown to ruby red color is produced, confirm for the presence of tin by reducing a portion with carbonate of soda and cyanide of potassium (§ 129, 11).

*β.* Triturate a small portion with finely pulverized quartz, moisten the mixture in a small crucible with a few drops of strong sulphuric acid and warm gently.

*aa. White fumes are evolved, which redden litmus, and render turbid a drop of water* (§ 150, 6): indicates FLUORIDE OF CALCIUM. Reduce a portion of the substance to a fine powder, decompose this in a platinum crucible with sulphuric acid, and try the reaction on glass (§ 146), to confirm the presence of FLUORINE; boil the residue with hydrochloric acid, filter, neutralize the filtrate with ammonia, and test for LIME with oxalate of ammonia.

*bb. No fumes are evolved which redden litmus, and render turbid a drop of water.* Mix a portion of the very finely pulverized substance with 4 times the quantity of pure carbonate of soda and potassa, and fuse in a platinum

* Graphite requires strong heating in a current of oxygen.

crucible (or on platinum foil). Boil the fused mass with water, filter should a residue be left, and wash the latter. Acidulate a portion of the filtrate with hydrochloric acid, and test with chloride of barium for SULPHURIC ACID; and in case you do not find that acid, test another portion of the filtrate for SILICIC ACID, by evaporating the fluid acidified with hydrochloric acid (§ 150, 2). If silicic acid also is absent, dissolve the residue of the evaporation in hydrochloric acid and test with ammonia for ALUMINA.

If the SILICIC ACID was present in the pure state, the mass resulting from the fusion with carbonate of soda and potassa must have dissolved in water to a clear fluid; but if silicates also happened to be present, the bases of them are left behind undissolved, and may be further examined.

In the absence of alumina you cannot expect the fusion to dissolve completely in water unless you have employed a large quantity of the flux and a high temperature.

If sulphuric acid has been found, the alkaline earth which was combined with it is found on the filter as a carbonate. Wash this, then dissolve in dilute hydrochloric acid, evaporate to dryness, take up with water, and test for BARYTA, STRONTIA, and LIME, as directed 62.

### *Complex Compounds.**

### A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

### *Detection of the Bases.†*

### § 189.‡

(*Treatment with Hydrochloric Acid: Detection of Silver, Suboxide of Mercury* [*Lead*].)

The systematic course for the detection of the bases is essen- 101
tially the same for bodies soluble in water, as for those which are soluble only in acids. Where the different nature of the original solution occasions a variation in the course of analysis, such variation will be distinctly stated.

#### I. SOLUTION IN WATER.

MIX THE PORTION INTENDED FOR THE DETECTION OF THE 102
BASES WITH SOME HYDROCHLORIC ACID.

* I use this term to designate compounds in which all the more frequently occurring bases, acids, metals, and metalloids are supposed to be present.

† Consult the explanations in the Third Section, with the contents of which you should make yourself thoroughly acquainted before proceeding further. Regard is here had also to the presence of the acids of arsenic, and of those salts of the alkaline earths which dissolve in hydrochloric acid, and separate again from that solution unaltered upon neutralisation of the acid by ammonia.

‡ Consult the remarks in the Third Section.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID.

*a.* NO PRECIPITATE IS FORMED: this indicates the absence of silver and suboxide of mercury. Pass on to § 190.

*b.* A PRECIPITATE IS FORMED. Add more hydrochloric acid, drop by drop, until the precipitate ceases to increase; then add about six or eight drops more of hydrochloric acid, shake the mixture and filter.

The precipitate produced by hydrochloric acid may consist of chloride of silver, subchloride of mercury, chloride of lead, a basic salt of antimony, basic chloride of bismuth, metachloride of tin, possibly also benzoic acid. The basic salt of antimony and the basic chloride of bismuth, however, redissolve in the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of chloride of silver, subchloride of mercury, or chloride of lead (possibly also of the very rare metachloride of tin and benzoic acid, which, however, are disregarded *here*).

Wash the precipitate collected upon the filter twice with cold water, add the washings to the filtrate, and examine the solution as directed § 190, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid (which indicates the presence of compounds of antimony or bismuth, or possibly also of metachloride of tin).

Treat the twice-washed precipitate on the filter as follows; 103

*α.* Pour hot water over it upon the filter, and test the fluid running off with hydrosulphuric acid and with sulphuric acid for LEAD. (The non-formation of a precipitate simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid fails to precipitate lead from dilute solutions). If the hydrochloric acid precipitate contains chloride of lead, wash it several times with hot water to dissolve out the lead.

*β.* If there is a residue remaining on the filter, treat it with ammonia. If this changes its color to black or gray, it is a proof of the presence of SUBOXIDE OF MERCURY.

*γ.* Add to the ammoniacal fluid running off in *β* nitric acid to strongly acid reaction. The formation of a white, curdy precipitate indicates the presence of SILVER.* (If the precipitate still contained lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic salt of lead. This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.)

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION. 104

*a.* THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A

* If the quantity of silver is only very small, its presence is indicated by opalescence of the fluid.

PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON FURTHER ADDITION OF HYDROCHLORIC ACID: pass on to § 190.

*b.* THE ADDITION OF HYDROCHLORIC ACID PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.

*a. The formation of the precipitate is attended neither with evolution of hydrosulphuric acid nor of hydrocyanic acid.* Filter, and treat the filtrate as directed § 190. 105

*aa.* THE PRECIPITATE IS WHITE. It may, in that case, consist of a salt of lead or silver, insoluble or difficultly soluble in water and hydrochloric acid (CHLORIDE OF LEAD, SULPHATE OF LEAD, CHLORIDE OF SILVER, &c.), or it may be HYDRATE OF SILICIC ACID. Test it for the bases and acids of these compounds as directed § 203, bearing in mind that the chloride of lead or chloride of silver which may be found may possibly have been formed in the process.

*bb.* THE PRECIPITATE IS YELLOW OR ORANGE. In that case it may consist of SULPHIDE OF ARSENIC, and if the fluid from which it has separated was not boiled long, or only with very dilute hydrochloric acid, also of SULPHIDE OF ANTIMONY, or BISULPHIDE OF TIN, which substances were originally dissolved in ammonia, potassa, soda, phosphate of soda, or some other alkaline fluid, with the exception of alkaline sulphides and cyanides. Examine the precipitate, which may also contain HYDRATE OF SILICIC ACID, as directed 40.

*β. The formation of the precipitate is attended with evolution of hydrosulphuric acid, but not of hydrocyanic acid.** 106

*aa.* THE PRECIPITATE IS OF A PURE WHITE COLOR, AND CONSISTS OF SEPARATED SULPHUR. In that case a SULPHURETTED ALKALINE SULPHIDE is generally present. The presence of such a body may be detected also by the yellow or brownish-yellow color of the alkaline solution, and the odor of hydride of sulphur, which accompanies that of the sulphuretted hydrogen on the addition of an acid. Boil, filter, and treat the filtrate as directed § 194, the precipitate as directed § 203.

*bb.* THE PRECIPITATE IS COLORED. In that case you may conclude that a METALLIC SULPHUR SALT is present, *i.e.*, a combination of an alkaline sulphur base with a metallic sulphur acid. The precipitate may accordingly consist of TERSULPHIDE OF GOLD, BISULPHIDE OF PLATINUM, BISULPHIDE OF TIN, SULPHIDE OF ARSENIC, or SULPHIDE OF ANTIMONY. It might, however, consist also of SULPHIDE OF MERCURY or of SULPHIDE OF COPPER or SULPHIDE OF NICKEL, or contain these substances, as the former will dissolve readily in sulphide of

* Should the odor of the evolved gas leave any doubt regarding the actual presence or absence of hydrocyanic acid, add some chromate of potassa to a portion of the fluid, previously to the addition of the hydrochloric acid.

potassium, and in small quantities in sulphide of ammonium, and the latter are slightly soluble in sulphide of ammonium. Filter, and treat the filtrate as directed § 194, the precipitate as directed **40**.

γ. *The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrosulphuric acid.* This indicates the presence of an ALKALINE CYANIDE, and, if the evolution of the hydrocyanic acid is attended with that of hydrosulphuric acid, also of an alkaline SULPHIDE. In that case the precipitate may, besides the compounds enumerated in α and β, contain many other substances (*e.g.*, cyanide of nickel, cyanide of silver, &c.). Boil, with further addition of hydrochloric acid, or of nitric acid, until the whole of the hydrocyanic acid is expelled, and treat the solution, or, if an undissolved residue has been left, the filtrate as directed § 190; and the residue (if any) according to § 203 or § 204. **107**

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. **108**

α. *The escaping gas smells of hydrosulphuric acid:* this indicates a SIMPLE ALKALINE SULPHIDE, or SULPHUR SALT WITH ALKALINE OR ALKALINE EARTHY BASE. Proceed as directed § 194.

β. *The escaping gas is inodorous:* in that case it is CARBONIC ACID which was combined with an alkali. Pass on to § 190.

γ. *The escaping gas smells of hydrocyanic acid* (no matter whether hydrosulphuric acid or carbonic acid is evolved at the same time or not). This indicates an ALKALINE CYANIDE. Boil until the whole of the hydrocyanic acid is expelled, then pass on to § 190.

## II. SOLUTION IN HYDROCHLORIC ACID OR IN NITROHYDROCHLORIC ACID.

Proceed as directed § 190.

## III. SOLUTION IN NITRIC ACID.

Dilute a small portion; should this produce turbidity or a precipitate (indicative of bismuth), add nitric acid until the fluid is clear again, then hydrochloric acid. **109**

1. NO PRECIPITATE IS FORMED. Absence of silver and suboxide of mercury. Treat the principal solution as directed § 190.

2. A PRECIPITATE IS FORMED. Treat a larger portion of the nitric acid solution in the same way, filter, and examine the precipitate as directed **103**, the filtrate as directed § 190.

## § 190.*

*(Treatment with Hydrosulphuric Acid. Precipitation of the Metallic Oxides of Group V., 2nd Division, and of Group VI.)*

ADD TO A *small* PORTION OF THE CLEAR ACID SOLUTION HYDROSULPHURIC ACID WATER, UNTIL THE ODOR OF HYDROSULPHURIC ACID IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY.

1. NO PRECIPITATE IS FORMED, even after the lapse of some time. Pass on to § 194, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,† are not present;‡ the absence of sesquioxide of iron and of chromic acid is also indicated by this negative reaction. **110**

2. A PRECIPITATE IS FORMED.

*a. The precipitate is of a pure white color*, light, and finely pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of SESQUIOXIDE OF IRON.§ None of the other metals enumerated in **110** can be present. Treat the principal solution as directed § 194. **111**

*b. The precipitate is colored.*

Add to the larger proportion of the acid or acidified solution, best in a small flask, hydrosulphuric acid water in excess, *i.e.*, until the fluid smells distinctly of it after shaking, and the precipitate ceases to increase upon continued addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the oxides present of Groups I.—IV.), for further examination according to § 194, and *thoroughly* wash‖ the precipitate, which contains the sulphides of the metals present of Groups V. and VI. **112**

In many cases, and more particularly where there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit hydrosulphuric acid gas through the solution DILUTED WITH WATER, instead of adding hydrosulphuric acid water. When arsenic is suspected it is also well to keep the fluid at about 70° during the transmission of the gas.

* Consult the remarks in the Third Section.

† Where the preliminary examination has led you to suspect the presence of arsenic acid, you must endeavour to obtain the most conclusive evidence of the absence of this acid; this may be done by allowing the fluid to stand for some time at a gentle heat (about 70°), or by heating it with sulphurous acid previous to the addition of the hydrosulphuric acid. (Compare § 133, 3.)

‡ In solutions containing much free acid the precipitates are frequently formed only after dilution with water.

§ Sulphur will precipitate also if sulphurous acid, or iodic acid, or bromic acid is present (which substances are not included in our analytical course), and also if chromic acid, or chloric acid, or free chlorine is present. In presence of chromic acid the separation of the sulphur is attended with reduction of the acid to sesquioxide of chromium, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 138.) The white sulphur suspended in the green solution looks at first like a green precipitate, which frequently tends to mislead beginners.

‖ Compare § 7.

If the precipitate is yellow, it consists principally of 113
sulphide of arsenic, bisulphide of tin, or sulphide of cadmium; if orange colored, this indicates sulphide of antimony; if brown or black, one at least of the following oxides is present; oxide of lead, teroxide of bismuth, oxide of copper, oxide of mercury, teroxide of gold, binoxide of platinum, protoxide of tin. However, as a yellow precipitate may contain small particles of an orange colored, a brown, or even a black precipitate, and yet its color not be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in 110 in any precipitate produced by hydrosulphuric acid, and to proceed accordingly as the next paragraph (§ 191) directs.

## § 191.*

*(Treatment of the Precipitate produced by Hydrosulphuric Acid with Sulphide of Ammonium; Separation of the 2nd Division of Group V. from Group VI.)*

INTRODUCE A SMALL PORTION OF THE THOROUGHLY WASHED 114
PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID IN THE ACIDIFIED SOLUTION INTO A TEST-TUBE,† ADD A LITTLE WATER, AND FROM TEN TO TWENTY DROPS OF YELLOW SULPHIDE OF AMMONIUM, AND EXPOSE THE MIXTURE FOR A SHORT TIME TO A GENTLE HEAT.‡

1. THE PRECIPITATE DISSOLVES COMPLETELY IN SULPHIDE 115
OF AMMONIUM (or SULPHIDE OF SODIUM, as the case may be); absence of the metals of Group V.—cadmium, lead, bismuth, copper, mercury. Treat the remainder of the precipitate (of which you have digested a portion with sulphide of ammonium) as directed § 192. If the precipitate produced by hydrosulphuric acid was so trifling that you have used the whole of it in treating with sulphide of ammonium, precipitate the solution obtained in that process by addition of hydrochloric acid, filter, wash the precipitate, and treat it as directed § 192.

2. THE PRECIPITATE IS NOT REDISSOLVED, OR AT LEAST NOT 116
COMPLETELY even on heating with more sulphide of ammonium

* Consult the notes in the Third Section.

† If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum or horn; but if you have only a very trifling precipitate, make a hole in the bottom of the filter, and rinse the precipitate into the test tube by means of the washing-bottle, wait until the precipitate has subsided, and then decant the water.

‡ If the solution contains copper, which is generally revealed by the colour of the fluid, and may be ascertained positively by testing with a clean iron rod (see § 120, 11), use sulphide of sodium instead of sulphide of ammonium (in which sulphide of copper is not absolutely insoluble, see § 120, 5), and boil the mixture. But if the fluid, besides copper, contains also oxide of mercury (the presence of which is generally sufficiently indicated by the several changes of color exhibited by the precipitate forming upon the addition of the hydrosulphuric acid water [§ 119, 3], and which, in doubtful cases, may be detected with positive certainty by testing a portion of the original solution acidified with hydrochloric acid with protochloride of tin), sulphide of ammonium must be used, although the separation of the sulphides of the antimony group from the sulphide of copper is not fully effected in such cases. Were sulphide of sodium used, the sulphide of mercury would dissolve in this reagent, which would *impede* the ulterior examination of the sulphides of the antimony group.

or sulphide of sodium, as the case may be): presence of metals of Group V. Dilute with 4 or 5 parts of water, filter, and mix the filtrate with hydrochloric acid in slight excess.

*a. A pure white turbidity is occasioned, owing to the separation of sulphur.* Absence of the metals of Group VI.—gold, platinum, tin, antimony, and arsenic.* Treat the rest of the precipitate (of which you have digested a portion with sulphide of ammonium) according to § 193.

*b. A colored precipitate is formed:* presence of metals of 117
Group VI. and of Group V. Treat the entire precipitate produced by hydrosulphuric acid as you have treated the portion, *i.e.* digest it with yellow sulphide of ammonium or, as the case may be, sulphide of sodium, let subside, pour the supernatant liquid on a filter, digest the residue in the tube once more with yellow sulphide of ammonium (or sulphide of sodium), and filter. Wash the residue† (containing the sulphides of Group V.), and treat it afterwards as directed § 193. Dilute the filtrate (which contains the metals of Group VI. in the form of sulphur salts), add hydrochloric acid to distinctly acid reaction, heat gently, filter off the precipitate, which contains the sulphides of the metals of Group VI. mixed with sulphur, wash thoroughly, and proceed as directed in the next paragraph (§ 192).

## § 192.‡

*(Detection of the Metals of Group VI.: Arsenic, Antimony, Tin, Gold, Platinum.)*

If the precipitate consisting of the sulphides of Group VI. has 118
a PURE YELLOW COLOR, this indicates principally arsenic and binoxide of tin; if it is distinctly ORANGE-YELLOW, antimony is sure to be present; if it is BROWN or BLACK, this denotes the presence of protoxide of tin, platinum, or gold.

Beyond these general indications the color of the precipitate affords no safe guidance. It is therefore always advisable to test a yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely

* That this inference becomes uncertain if the precipitate produced by hydrosulphuric acid, instead of being digested with a small quantity of sulphide of ammonium, has been treated with a large quantity of that reagent, is self-evident; for the large quantity of sulphur which separates in that case will of course completely conceal any slight traces of sulphide of arsenic or bisulphide of tin which may have been thrown down. Compare also notes to § 190 and § 191 in the Third Section.

† If the residue suspended in the fluid containing sulphide of ammonium, and insoluble therein, subsides readily, it is not transferred to the filter, but washed in the tube by decantation. But if its subsidence proceeds slowly and with difficulty, it is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a washing-bottle; the application of a gentle heat will now materially aid the subsidence of the residue, and the supernatant water may then be decanted. The sulphides are occasionally suspended in the fluid in a state of such minute division that the fluid cannot be filtered off clear. In cases of the kind some chloride of ammonium should be added to the fluid, and it should be allowed to settle at a gentle heat for some time before being filtered.

‡ Consult the notes in the Third Section.

hidden by a large quantity of bisulphide of tin or sulphide of arsenic. Proceed accordingly as follows:

Heat a little of the precipitate on the lid of a porcelain crucible, or on a piece of porcelain or glass.*

119 1. *Complete volatilization ensues:* probable presence of ARSENIC, absence of the other metals of Group VI. Confirm by reduction of a portion of the precipitate with cyanide of potassium and carbonate of soda (§ 132, 12).† Whether that metal was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the methods described § 134, 9.

120 2. *A fixed residue is left.* In that case all the metals of Group VI. must be sought for. Dry the remainder of the precipitate thoroughly upon the filter, triturate it with about 1 part of anhydrous carbonate of soda and 1 part of nitrate of soda, and transfer the mixture in small portions at a time to a porcelain crucible, in which you have previously heated 2 parts of nitrate of soda to fusion.‡ As soon as complete oxidation is effected, pour the mass on to a piece of porcelain. After cooling soak the fused mass§ (the portion still sticking to the inside of the crucible as well as the portion poured out on the porcelain) in cold water, filter from the insoluble residue —which will remain if the mass contained antimony, tin, gold, or platinum—and wash thoroughly with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the solution of the antimonate of soda. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

121 *a.* EXAMINATION OF THE FILTRATE FOR ARSENIC (which must be present in it in the form of arsenate of soda). Add nitric acid to the fluid to distinct acid reaction,‖ heat to expel carbonic acid and nitrous acid, then divide the fluid into two portions. Add to the one portion some nitrate of silver (not too little), filter (in case chloride of silver¶ or nitrite of silver

* That this preliminary examination may be omitted if the precipitate has any other color than yellow, and that it can give a decisive result only if the precipitate has been thoroughly washed, is self-evident.

† In cases where the precipitate contains much free sulphur, dissolve the sulphide of arsenic which may be present, by digestion in carbonate of ammonia, filter, evaporate the solution with addition of a small quantity of carbonate of soda, to dryness, and heat the residue with cyanide of potassium and carbonate of soda.

‡ Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these with some carbonate and nitrate of soda, and project both the powder and the paper into the fusing nitrate of soda. It is *preferable*, however, in such cases, to procure, if practicable, a larger amount of the precipitate, as otherwise there will be but little hope of effecting the positive detection of all the metals of Group VI.

§ Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of antimonate and arsenate of soda, binoxide of tin, metallic gold and platinum, sulphate, carbonate, nitrate, and some nitrite of soda. Compare also § 134, 1. When gold and tin are present together the fused mass often has a peculiar light red color.

‖ In some cases where a somewhat large proportion of carbonate of soda has been used, or a very strong heat applied, a trifling precipitate (hydrated binoxide of tin) may separate upon the acidification of the filtrate with nitric acid. This may be filtered off, and then treated in the same manner as the undissolved residue.

¶ Chloride of silver will separate if the reagents were not perfectly pure, or the precipitate has not been thoroughly washed.

should have separated), pour upon the filtrate, along the side of the tube held slanting, a layer of dilute solution of ammonia—2 parts of water to 1 part of solution of ammonia—and allow to stand some time without shaking. The formation of a reddish-brown precipitate, which appears hovering cloud-like between the two layers (and may be seen far more readily and distinctly by reflected than by transmitted light), denotes the presence of ARSENIC.

If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, the fluid being stirred during this process, the precipitate of arsenate of silver which forms imparts a brownish-red tint to the entire fluid.

122 Add to the other portion of the acidified solution, first ammonia, then a mixture of sulphate of magnesia and chloride of ammonium, and rub the sides of the vessel with a glass rod. A crystalline precipitate of arsenate of magnesia and ammonia, which often forms only after long standing, and is deposited more particularly on the side of the vessel, shows the presence of arsenic. By way of confirmation the precipitate may be washed with water containing ammonia, dissolved in dilute hydrochloric acid and the solution precipitated by sulphuretted hydrogen with the aid of a gentle heat, or the arsenic may be reduced to the metallic state (compare § 132 and § 133). Whether the arsenic was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the methods described § 134, 9.

123 *b.* EXAMINATION OF THE RESIDUE FOR ANTIMONY, TIN, GOLD, PLATINUM. (As the antimony, if present in the residue, must exist as white pulverulent antimonate of soda, the tin as white flocculent binoxide, the gold and platinum in the metallic state, the appearance of the residue is in itself indicative of its nature. But it must be noted that on account of the slight solubility of sulphide of copper in sulphide of ammonium, a little oxide of copper may also be present in this residue.) Transfer the precipitate to the lid of a platinum crucible, or to a platinum capsule, heat with hydrochloric acid, add a little water, and throw in a small compact lump of pure zinc (more particularly, free from lead), no matter whether the precipitate has completely dissolved or not in the hydrochloric acid. This operation leaves the gold and platinum in the same state in which the fused mass contained them, viz., in the metallic state, to which the tin and antimony are now likewise reduced by the action of the zinc. The ANTIMONY reveals its presence at once, or after a short time, by blackening the platinum. As soon as the disengagement of hydrogen has nearly stopped, take out the lump of zinc, remove the solution of chloride of zinc by cautious decantation, warm the metals with hydrochloric acid, and test the solution—which, if TIN is present, must contain protochloride of tin—with chloride of mercury (§ 129, 8). In what state of oxidation tin or antimony were originally present may be ascertained according to § 134, 7 and 8.

After removing the tin by repeated boiling with hydrochloric 124
acid, and all the hydrochloric acid by thoroughly washing with water, examine the insoluble residue (if one is left) as follows: Heat it in the platinum lid with some water, with addition of a few grains of tartaric acid, then add some nitric acid, and heat gently. If the residue dissolves completely, no gold or platinum is present; if a residue is left undissolved, you must test it for these metals. For this purpose remove the acid solution (which may be tested again for ANTIMONY with hydrosulphuric acid) by decantation and washing, transfer the residue to a porcelain dish, heat with a little aqua regia, evaporate the solution to a small volume, and test for GOLD and PLATINUM as directed § 128.

## § 193.*

(*Detection of the Metallic Oxides of Group V., 2nd Division:—Oxide of Lead, Teroxide of Bismuth, Oxide of Copper, Oxide of Cadmium, Oxide of Mercury.*)

THOROUGHLY WASH THE PRECIPITATE WHICH HAS NOT BEEN 125
DISSOLVED BY SULPHIDE OF AMMONIUM, AND BOIL WITH DILUTE NITRIC ACID. This operation is performed best in a small porcelain dish: the boiling mass must be constantly stirred with a glass rod. A great excess of acid must be avoided.

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS 126
FLOATING IN THE FLUID ONLY THE SEPARATED LIGHT FLOCCULENT AND YELLOW SULPHUR: this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH may be present. Filter from the separated sulphur, and treat the filtrate as follows (should there be too much nitric acid present, the greater part of this must first be driven off by evaporation). Add to a portion of the filtrate dilute sulphuric acid in moderate quantity, heat gently, and allow to stand some time.

*a.* NO PRECIPITATE FORMS: absence of lead. Mix the 127
remainder of the filtrate with ammonia in excess, and gently heat.

*a. No precipitate is formed:* absence of bismuth. If the 128
liquid is blue, COPPER is present; very minute traces of copper, however, might be overlooked if the color of the ammoniated fluid alone were consulted. To be quite safe, and also to test for cadmium, evaporate the ammoniated solution nearly to dryness, add a little acetic acid, and, if necessary, some water, and

*aa.* Test a small portion of the fluid for copper with 129
ferrocyanide of potassium. A reddish-brown precipitate, or a light brownish-red turbidity, indicates COPPER (in the latter case only to a very trifling amount).

*bb.* To the remainder if copper is absent add hydro- 130
sulphuric acid. A yellow precipitate indicates CADMIUM. If copper is present, it is most conveniently removed in the form of subsulphocyanide by means of sulphurous acid and sulphocyanide of potassium, and the filtrate,

* Consult the notes in the Third Section.

after being evaporated to drive off excess of sulphurous acid, is tested for cadmium with hydrosulphuric acid. Or both metals may be precipitated by hydrosulphuric acid and then separated by cyanide of potassium (in which case the sulphides must have been recently precipitated) or by boiling dilute sulphuric acid (§ 123).

*β. A precipitate is formed.* BISMUTH is present. Filter 131
and test the filtrate for copper and cadmium as directed **128**. To test the washed precipitate more fully for bismuth, slightly dry the filter containing it between blotting-paper, remove the still moist precipitate with a platinum spatula or a knife, dissolve on a watch-glass in the *least possible quantity* of hydrochloric acid, and then add water. The appearance of a milky turbidity confirms the presence of bismuth.

*b.* A PRECIPITATE IS FORMED. Presence of LEAD. Mix 132
the whole of the nitric acid solution in a porcelain dish with a sufficient quantity of dilute sulphuric acid, evaporate on the water-bath until the nitric acid is expelled, dilute the residue with some water containing sulphuric acid, filter off at once the sulphate of lead left undissolved, and test the filtrate for bismuth, copper, and cadmium, as directed **127**.* Test the precipitate, after washing, by one of the methods in § 123.

2. THE PRECIPITATE OF THE SULPHIDES DOES NOT COM- 133
PLETELY DISSOLVE IN THE BOILING NITRIC ACID, BUT LEAVES A RESIDUE, BESIDES THE SULPHUR THAT FLOATS IN THE FLUID. Probable presence of OXIDE OF MERCURY (which may be pronounced almost certain if the precipitate is heavy and black). Allow the precipitate to subside, filter off the fluid, which is still to be tested for CADMIUM, COPPER, LEAD, and BISMUTH; mix a small portion of the filtrate with a large amount of solution of hydrosulphuric acid, and should a precipitate form or a coloration become visible, treat the remainder of the filtrate according to **126**.

Wash the residue (which may, besides sulphide of mercury, also contain sulphate of lead, formed by the action of nitric acid upon sulphide of lead, and also binoxide of tin, and possibly sulphide of gold and sulphide of platinum, as the separation of the sulphides of tin, gold, and platinum from the sulphides of the metals of the fifth group is often incomplete), and examine one half of it for mercury,† by dissolving it in some hydrochloric acid, with addition of a very small portion of chlorate of potassa, and testing the solution with copper or protochloride of tin (§ 119); fuse the other half with cyanide of potassium and carbonate of soda, and treat the fused mass with water. If metallic grains remain, or if a metallic powder is left undissolved, wash this residue, heat with nitric acid, and test the solution obtained with sulphuric acid for lead. Wash the residue which the nitric acid may leave undissolved, and extract from it any hydrate of metastannic acid which

* For another method of separating cadmium, copper, lead, and bismuth, see the Third Section.

† If you have an aqueous solution, or a solution in very dilute hydrochloric acid, the oxide of mercury found was present in the original substance in that form; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid or aqua regia, the mercury may have been originally present in the form of suboxide.

it may contain, according to § 130, 1, as metastannic chloride. Should a metallic powder be left undissolved in the process, heat it with aqua regia, and test the solution for gold and platinum as directed § 128.

## § 194.*

*(Precipitation with Sulphide of Ammonium, Separation and Detection of the Oxides of Groups III. and IV.: Alumina, Sesquioxide of Chromium; Oxide of Zinc, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Proto- and Sesquioxide of Iron; and also of those Salts of the Alkaline Earths which are precipitated by Ammonia from their Solution in Hydrochloric Acid: Phosphates, Borates, Oxalates, Silicates, and Fluorides.)*

134 PUT A *small portion* OF THE FLUID IN WHICH HYDROSULPHURIC ACID HAS FAILED TO PRODUCE A PRECIPITATE (110), OR OF THE FLUID WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED (112), in a test-tube, observe whether it is colored or not,† boil to expel the hydrosulphuric acid which may be present, add a few drops of nitric acid, boil, and observe again the color of the fluid; then cautiously add ammonia just to alkaline reaction, heat, observe whether this produces a precipitate, then add some sulphide of ammonium, no matter whether ammonia has produced a precipitate or not.

135 *a.* NEITHER AMMONIA NOR SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE. Pass on to § 195, for iron, nickel, cobalt, zinc, manganese, sesquioxide of chromium, alumina, are not present,‡ nor are phosphates, borates,§ silicates, and oxalates‖ of the alkaline earths; nor fluorides of the metals of the alkaline earths, nor silicic acid—originally in combination with other bases.

136 *b.* SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE, AMMONIA HAVING FAILED TO DO SO: absence of phosphates, borates,§ silicates, and oxalates‖ of the alkaline earths; of the fluorides of the metals of the alkaline earths; of silicic acid, originally in combination with other bases; and also, if no organic matters are present, of iron, sesquioxide of chromium, and alumina. Pass on to **138**.

* Compare the notes in the Third Section.

† If the fluid is colorless, it contains no chromium. If colored, the tint will to some extent act as a guide to the nature of the substance present; thus a green tint, or a violet tint turning green upon boiling, points to chromium; a light green tint to nickel; a reddish color to cobalt; the turning yellow of the fluid upon boiling with nitric acid to iron. It must, however, be always borne in mind that these tints are perceptible only if the metallic oxides are present in large quantity, and also that complementary colors, such as, for instance, the green of the nickel solution and the red of the cobalt solution will destroy each other, and that, accordingly, a solution may contain both metals and yet appear colorless.

‡ This only holds good as regards alumina and sesquioxide of chromium in the absence of non-volatile organic substances, especially acids such as citric and tartaric acids. Citric acid may also prevent the precipitation of manganese. Compare p. 239, footnote.

§ Presence of much chloride of ammonium has a great tendency to prevent the precipitation of borates of the alkaline earths.

‖ Oxalate of magnesia is thrown down from hydrochloric acid solution by ammonia after some time only, and never completely; dilute solutions are not precipitated by ammonia.

*c.* AMMONIA PRODUCES A PRECIPITATE before the addition of sulphide of ammonium. The course of proceeding to be pursued now depends upon whether, (*a*) the original solution is simply aqueous, and has a neutral reaction, or (*β*) the original solution is acid or alkaline. In the former case pass on to **138**, since phosphates, borates, oxalates, and silicates of the alkaline earths, fluorides of the metals of the alkaline earths, and silicic acid in combination with other bases, cannot be present. In the latter case regard must be had to the possible presence of all the bodies enumerated in **135**, and also, in the presence of organic matter, of the combinations of alkaline earths with citric and tartaric acids; pass on to **150**. 137

1. DETECTION OF THE BASES OF GROUPS III. AND IV. IF PHOSPHATES, &C., OF THE ALKALINE EARTHS ARE NOT PRESENT.* 138

Mix the fluid mentioned at the beginning of **134**, a portion of which you have submitted to a preliminary examination, with some chloride of ammonium, then with ammonia, just to alkaline reaction, lastly with sulphide of ammonium until the fluid, after being shaken, smells distinctly of that reagent; shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the FILTRATE,† which may contain bases of Groups II. and I., for subsequent examination according to § 195. Wash the PRECIPITATE with water to which a very little sulphide of ammonium has been added, then proceed with it as follows:—

*a.* IT HAS A PURE WHITE COLOR: absence of iron, cobalt, nickel. You must test it for all the other bases of Groups III. and IV., as the faint tints of sesquioxide of chromium and sulphide of manganese are imperceptible in a large quantity of a white precipitate. Dissolve the precipitate by heating it in a small dish with the least possible amount of hydrochloric acid; boil—should hydrosulphuric acid be evolved—until this is completely expelled, concentrate by evaporation to a small‡ bulk, add concentrated solution of soda in excess, heat to boiling, and keep for some time in a state of ebullition. 139

*a. The precipitate formed at first dissolves completely in the excess of soda.* Absence of manganese and chromium, presence of alumina or oxide of zinc. Test a portion of the alkaline solution with solution of hydrosulphuric acid (a little, not excess) for ZINC; acidify the remainder with hydrochloric acid, add ammonia *slightly* in excess, and apply heat. A 140

* This simpler method will fully answer the purpose in most cases; for very accurate analysis the method beginning at 150 is preferable, as this will permit also the detection of minute quantities of alkaline earths, which may have been thrown down together with alumina or sesquioxide of chromium. Solutions which are distinctly colored by chromium should always be examined by 150.

† If the filtrate has a brownish color, this points to nickel, sulphide of nickel, as is well known, being, under certain circumstances, slightly soluble in sulphide of ammonium; this, however, involves no modification of the analytical course.

‡ Compare § 106, 6.

white flocculent precipitate insoluble in more chloride of ammonium, indicates ALUMINA.*

*β. The precipitate formed does not dissolve, or dissolves only* 141
*partially in the excess of soda.* Dilute, filter, and test the FILTRATE, as in 140, for ZINC and ALUMINA. With the undissolved PRECIPITATE, which, if containing manganese, looks brown or brownish, proceed as follows:—

*aa.* If the color of the solution gives you no reason to suspect the presence of chromium, test the precipitate for MANGANESE, with carbonate of soda in the outer blow-pipe flame.

*bb.* But where the color of the solution indicates chro- 142
mium, the examination of the residue insoluble in solution of soda is more complicated, since it may in that case contain also oxide of zinc, possibly even the whole quantity present of this metal (§ 112). Dissolve the precipitate therefore in hydrochloric acid, evaporate the solution to a small residue, dilute, nearly neutralize the free acid with carbonate of soda, add carbonate of baryta in slight excess, allow to digest in the cold until the fluid has become colorless, filter, and test the precipitate for CHROMIUM, by fusion with carbonate of soda and chlorate of potassa (§ 102, 8). Remove the baryta from the filtrate, by precipitating with some sulphuric acid, filter, evaporate to a small residue, add concentrated solution of potassa or soda in excess, and test the filtrate for ZINC with hydrosulphuric acid, the precipitate, if any, for MANGANESE as in *aa.*

*b.* IT IS NOT WHITE: this indicates chromium, manganese, 143
iron, cobalt, or nickel. If it is black, or inclines to black, one of the three metals last-mentioned is present. Under any circumstances all the oxides of Groups III. and IV. must be looked for.

Remove the washed precipitate from the filter with a spatula, or by rinsing it with the aid of a washing-bottle through a hole made in the bottom of the filter, into a test-tube, and pour over it rather dilute cold hydrochloric acid (1 part of hydrochloric acid sp. gr. 1·12 with about 5 parts of water) in moderate excess.

*a. It dissolves completely* (except perhaps a little sulphur 144
which may separate); absence of cobalt and nickel, at least of notable quantities of these two metals.

Boil until the hydrosulphuric acid is *completely* expelled, add nitric acid, boil, filter if particles of sulphur are suspended in the fluid, concentrate by evaporation to a small residue, add concentrated solution of potassa or soda in excess, boil, filter the fluid from the insoluble precipitate which is sure to remain, wash the latter, and proceed first to examine the filtrate, then the precipitate.

* It is of course assumed that the soda or potassa used is free from alumina and silicic acid. In the contrary case you may make a counter experiment with a similar quantity of the alkali alone; if you obtain a very much smaller precipitate now than you obtained in the analysis you may conclude that alumina is actually present in the substance.

*aa.* Test a small portion of the *filtrate* with hydrosulphuric acid for ZINC; acidify the remainder with hydrochloric acid, then test with ammonia for ALUMINA. Compare **140**. **145**

*bb.* Dissolve a small portion of the *precipitate* in hydrochloric acid and test with ferrocyanide of potassium added drop by drop, or with sulphocyanide of potassium for IRON.* Test another portion for CHROMIUM by fusing with carbonate of soda and chlorate of potassa, and boiling the fusion with water (§ 102, 8).† If no chromium has been found, examine the remainder for MANGANESE, by carbonate of soda in the oxidizing flame. If chromium is present, on the other hand, test the remainder of the precipitate for manganese and zinc as directed **142**. (Under these circumstances the whole of the zinc may be present in this precipitate.) **146**

*β. The precipitate is not completely dissolved, a black residue being left.* This indicates COBALT and NICKEL. This indication is not certain, especially in the presence of much sulphide of iron, particles of which may become enveloped in the separated sulphur and thus be protected from the action of the hydrochloric acid. Filter, wash, and examine the filtrate according to **144**. Heat the precipitate with the filter in a porcelain crucible till the filter is incinerated, allow to cool, warm with hydrochloric acid and a drop or two of nitric acid, add water, then ammonia in moderate excess, and filter. **147**

The ammoniacal filtrate will be blue in presence of much nickel, brownish in the presence of much cobalt, and will have a less distinct mixed color if both metals are present. Test a portion of it with sulphide of ammonium. If a black precipitate is formed, which does not redissolve on acidifying with hydrochloric acid, the presence of cobalt or nickel is proved.

In that case evaporate the rest of the ammoniacal solution to dryness, drive off the ammonia salts by gentle ignition, and proceed with the residue as follows:—

*aa.* Test a small portion of it with borax, first in the outer, then in the inner blowpipe-flame. If the bead in the oxidizing flame is violet whilst hot, and of a pale reddish-brown when cold, and turns in the reducing flame gray and turbid, NICKEL is present; but if the color of the bead is blue in both flames, and whether hot or cold, COBALT is present. As in the latter case the presence of nickel cannot be distinctly recognised, examine **148**

* Since Prussian blue dissolves in ferrocyanide of potassium to a colorless fluid, small quantities of iron may easily be overlooked if the ferrocyanide is added rapidly in large quantity. If iron is found, the original solution must be tested with ferricyanide of potassium and sulphocyanide of potassium to see in what state of oxidation it is actually present.

† If the solution is green from the presence of manganate of soda, heat it with a few drops of alcohol and filter off the peroxide of manganese formed.

*bb.* the remainder of the residue by dissolving it in hydrochloric acid and a little nitric acid, evaporating nearly to dryness, and adding nitrite of potassa and, lastly, acetic acid (§ 109, 14). If a yellow precipitate forms, after standing for some time at a gentle heat, this confirms the presence of COBALT. Filter after about twelve hours, and test the filtrate with solution of soda for NICKEL. 149

2. DETECTION OF THE BASES OF GROUPS III. AND IV. IN CASES WHERE PHOSPHATES, BORATES, OXALATES, SILICATES (IN THE PRESENCE OF ORGANIC MATTER, POSSIBLY ALSO TARTRATES AND CITRATES,) OF THE ALKALINE EARTHS, FLUORIDES OF THE METALS OF THE ALKALINE EARTHS, OR HYDRATE OF SILICIC ACID, MAY POSSIBLY HAVE BEEN THROWN DOWN WITH THESE BASES, *i.e.*, in cases where the original solution was acid or alkaline, and a precipitate was produced by ammonia in the preliminary examination of **134**. 150

Mix the fluid mentioned in **134** with some chloride of ammonium, then with ammonia just to alkaline reaction, lastly with sulphide of ammonium until the fluid, after being shaken, smells distinctly of the reagent; shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the FILTRATE, which may contain bases of Groups II. and I., for subsequent examination according to § 195. Wash the PRECIPITATE with water to which a very little sulphide of ammonium has been added, then proceed with it as directed **152**. To give a clear notion of the obstacles to be overcome in this analytical process, I must remind you that it is necessary to examine the precipitate for the following bodies: Iron, nickel, cobalt (these show their presence to a certain extent by the black or blackish color of the precipitate), manganese, zinc, sesquioxide of chromium (the latter generally reveals its presence by the color of the solution), alumina; baryta, strontia, lime, magnesia, which latter substances may have fallen down in combination with phosphoric acid, boracic acid, oxalic acid, silicic acid, in form of fluorides, or in combination with sesquioxide of chromium. Besides these bodies, hydrate of silicic acid, and free sulphur may be present. (In the presence of organic substances, tartrates and citrates of alkaline earths may be also present.)

As the original substance must be afterwards examined for all acids that might possibly be present, it is not *indispensable* to test for the above enumerated acids at this stage; still, as it is often interesting to detect these acids at once, especially in cases where a somewhat large proportion of some alkaline earth has been found in this precipitate, a method for the detection of the acids in question will be found appended by way of supplement to the method for the detection of the bases. 151

As soon as the washing is finished, remove the precipitate from the filter with a small spatula, or with the washing bottle, and pour over it cold dilute hydrochloric acid (1 part of hydrochloric acid sp. gr. 1·12, with about 5 parts of water) in moderate excess. 152

RESIDUE REMAINS. Filter, and treat the filtrate as 153.

directed **154**. The residue, if it is black, may contain sulphide of nickel and sulphide of cobalt and, besides these, sulphur and silicic acid, possibly also fluoride of calcium, (which is rather difficultly soluble). Wash, and examine a sample of it with phosphate of soda and ammonia before the blowpipe, in the outer flame. If a silica skeleton remains undissolved (§ 150, 8), this proves the presence of SILICIC ACID; the color of the bead will generally at once indicate COBALT or NICKEL, compare **148**. Incinerate the rest of the precipitate and test it first for FLUORINE, by heating with sulphuric acid (§ 146, 5). If fluorine is present, on treating the residue with a little water, and adding an equal volume of alcohol, sulphate of LIME will remain behind. Finally, if the color of the microcosmic bead has been ambiguous, remove the alcohol from the sulphuric acid solution by evaporation (if necessary), precipitate the traces of iron generally present by ammonia, and test for nickel and cobalt as in **147** to **150**.

*b*. NO RESIDUE IS LEFT (except a little sulphur, whose purity is to be proved by washing, drying, and burning): absence of nickel and cobalt, at least in any notable proportion. **154**

Boil the solution until the sulphuretted hydrogen is expelled, filter if necessary, and then proceed as follows:

*a*. Mix a small portion of the solution with dilute sulphuric acid. If a precipitate forms, this may consist of sulphates of BARYTA and STRONTIA, possibly also of sulphate of lime. Filter, wash the precipitate, and examine it either by the coloration of flame (see § 99, at end), or decompose it by boiling or fusing with carbonated alkali, wash the carbonates produced, dissolve them in hydrochloric acid, evaporate to dryness, take up with water, and test the solution as directed **164**. Mix the fluid which has not been precipitated by dilute sulphuric acid, or the fluid filtered from the precipitate produced, with 3 volumes of spirit of wine. If a precipitate forms, this consists of sulphate of LIME. Filter, dissolve in water, and add oxalate of ammonia to confirm the presence of lime. **155**

*β*. Heat a somewhat larger sample with some nitric acid, and test a small portion of the fluid with ferrocyanide of potassium added drop by drop, or with sulphocyanide of potassium for IRON;* mix the remainder with sesquichloride of iron† in sufficient quantity to make a drop of fluid give a yellowish precipitate when mixed on a watch-glass with a drop of ammonia, evaporate on a water-bath to a small bulk, add some water, then a few drops of carbonate of soda, just sufficient to *nearly* neutralize the free acid, and lastly carbonate of baryta in slight excess, stir, and allow to stand in the cold until the fluid above the precipitate **156**

* Whether the iron was present as sesquioxide or as protoxide, must be ascertained by testing the original solution in hydrochloric acid with ferricyanide of potassium and sulphocyanide of potassium.

† The addition of sesquichloride of iron is necessary, to effect the separation of phosphoric acid and silicic acid which may be present.

has become colorless. Filter the precipitate (*aa*) from the solution (*bb*), and wash.

*aa.* Boil the *precipitate* for some time with solution of soda, filter, and test the filtrate for ALUMINA,* by acidifying with hydrochloric acid, adding ammonia to alkaline reaction and boiling. The part of the precipitate insoluble in solution of soda is examined for CHROMIUM, by fusion with chlorate of potassa and carbonate of soda (§ 102, 8). 157

*bb.* Mix the *solution* first with a few drops of hydrochloric acid, boil to expel the whole of the carbonic acid, then add some ammonia and sulphide of ammonium.

*aa. No precipitate forms:* absence of manganese and zinc. Mix the solution containing chloride of barium with dilute sulphuric acid in slight excess, boil, filter, supersaturate with ammonia, and mix with oxalate of ammonia. If a precipitate of oxalate of lime forms, filter, and test the filtrate with phosphate of soda for MAGNESIA. 158

*ββ. A precipitate forms.* Filter, and proceed with the filtrate according to **158**. The precipitate may contain sulphide of manganese, sulphide of zinc, traces of sulphide of cobalt and sulphide of nickel; and also (in the presence of tartrates and citrates of the alkaline earths) sulphide of iron. Wash it and test for MANGANESE, ZINC, COBALT, and NICKEL, according to **143—150** (if the last two metals have not been found in **153**). 159

γ. If you have found alkaline earths in α and β, and wish to know the acids in combination with which they have passed into the precipitate produced by sulphide of ammonium, this may be ascertained by making the following experiments with the remainder of the hydrochloric acid solution of the sulphide of ammonium precipitate. 160

*aa.* Evaporate a small portion in a dish or watch-glass on the water-bath to complete dryness, then treat with hydrochloric acid. If there was any SILICIC ACID in the solution, this will be left undissolved. Evaporate the solution with nitric acid and test it for PHOSPHORIC ACID, by means of molybdic acid (§ 142, 10). 161

*bb.* Concentrate another portion by evaporation, mix it with carbonate of soda *in excess*, boil for some time, filter, and examine one portion of the filtrate for OXALIC ACID, by acidifying with acetic acid and adding solution of sulphate of lime; another portion for BORACIC ACID, by slightly acidifying with hydrochloric acid, and testing

* If the solution or the soda contains silicic acid, the precipitate taken for alumina may also contain silicic acid. A simple trial with phosphate of soda and ammonia, on a platinum wire, in the blowpipe flame, will show whether the precipitate really contains silicic acid. Should this be the case, ignite the remainder of the supposed alumina precipitate on the lid of a platinum crucible, add some acid sulphate of potassa, fuse and treat with hydrochloric acid, which will dissolve the alumina, leaving *the silicic* acid undissolved; precipitate the alumina from the solution by ammonia.

with turmeric-paper (§ 144 and § 145). (In the presence of organic matter the rest of the filtrate may be used for testing for TARTARIC and CITRIC ACIDS, compare **198**.)

*cc.* Precipitate the remainder with ammonia, filter, wash and dry the precipitate, and examine it for FLUORINE according to § 146, 5. **162**

## § 195.*

(*Separation and Detection of the Oxides of Group II. which are precipitated by Carbonate of Ammonia in Presence of Chloride of Ammonium, viz., Baryta, Strontia, Lime.*)

TO A SMALL PORTION OF THE FLUID IN WHICH AMMONIA AND SULPHIDE OF AMMONIUM HAVE FAILED TO PRODUCE A PRECIPITATE (**135**), OR OF THE FLUID FILTERED FROM THE PRECIPITATE FORMED, ADD CHLORIDE OF AMMONIUM, IF THE SOLUTION CONTAINS NO AMMONIACAL SALT, THEN CARBONATE OF AMMONIA AND SOME CAUSTIC AMMONIA, AND HEAT FOR SOME TIME VERY GENTLY (not to boiling).

1. NO PRECIPITATE FORMS: absence of any notable quantity of baryta, strontia, and lime. Traces of these alkaline earths may, however, be present; to detect them proceed as follows. Add to another portion of the fluid some sulphate of ammonia (prepared by supersaturating dilute sulphuric acid with ammonia); if the fluid becomes turbid, it contains traces of baryta. Add to a third portion some oxalate of ammonia and allow it to stand; if the fluid turns turbid, traces of lime are present. Treat the remainder of the fluid as directed § 196, after having previously removed the traces of lime and baryta which may have been found, by means of the reagents that have served to effect their detection. **163**

2. A PRECIPITATE IS FORMED. Presence of LIME, BARYTA, or STRONTIA. Treat the whole fluid of which a portion has been tested with ammonia, and carbonate of ammonia, the same as the sample, filter off the precipitate formed, after gently heating, and test portions of the filtrate with sulphate and oxalate of ammonia for traces of lime and baryta, which it may possibly still contain; remove such traces, should they be found, by means of the said reagents, and examine the fluid, thus perfectly freed from baryta, strontia, and lime, for magnesia, according to § 196. Wash the precipitate produced by carbonate of ammonia, dissolve it in the least possible amount of dilute hydrochloric acid, evaporate to dryness on the water-bath, take up the residue with *a little* water, and add to a small portion of the fluid a sufficient quantity of solution of sulphate of lime. **164**

*a. No precipitate is formed*, EVEN AFTER THE LAPSE OF SOME TIME. Absence of baryta and strontia;† presence of LIME. To confirm mix another sample with oxalate of ammonia.

* Compare the notes in the Third Section.

† Very minute traces of strontia cannot be detected in this way, as the sulphate of strontia is not absolutely insoluble. See § 99.

*b. A precipitate is formed by solution of sulphate of lime.*

*a. It is formed immediately;* this indicates BARYTA. 165
Besides this, strontia and lime may also be present.

Evaporate the remainder of the hydrochloric acid solution of the precipitate produced by carbonate of ammonia to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved chloride of barium, dilute with an equal volume of water, mix with a few drops of hydrofluosilicic acid—which will throw down the small portion of baryta that had dissolved in form of chloride of barium—allow to stand for some time; filter, and mix the filtrate with dilute sulphuric acid. The formation of a precipitate indicates the presence of strontia or lime, or of both. Filter after some time, and test the precipitate according to p. 97 for STRONTIA and LIME. The separation by boiling the sulphates with sulphate of ammonia suffices for ordinary cases; but in very delicate analyses the nitrates must be treated with alcohol and ether, and the residue examined in the spectroscope.

*β. It is formed only after some time.* Absence of baryta, 166
presence of STRONTIA. Mix the remainder of the aqueous solution of the chlorides with a sufficient amount of concentrated solution of sulphate of ammonia, and boil for some time, renewing the water as it evaporates, and adding ammonia to keep the fluid alkaline. Then filter off the sulphate of strontia, and test the filtrate for LIME, with oxalate of ammonia.

## § 196.

### (*Examination for Magnesia.*)

TO A PORTION OF THE FLUID IN WHICH CARBONATE, SULPHATE, AND OXALATE OF AMMONIA HAVE FAILED TO PRODUCE A PRECIPITATE (163) OR OF THE FLUID FILTERED FROM THE PRECIPITATES FORMED (164), ADD AMMONIA, THEN SOME PHOSPHATE OF SODA, AND, SHOULD A PRECIPITATE NOT AT ONCE FORM, RUB THE INNER SIDES OF THE TEST TUBE WITH A ROD, AND LET THE MIXTURE STAND FOR SOME TIME.

1. NO PRECIPITATE IS FORMED: absence of magnesia. Evap- 167
orate another portion of the fluid to dryness (preferably in the lid of a platinum crucible), and ignite gently. *If a residue remains,* treat the remainder of the fluid the same as the sample, and examine the residue, which by the moderate ignition to which it has been subjected has been freed from ammonia, for potassa and soda, according to § 197. *If no residue is left,* this is a proof of the absence of the fixed alkalies; pass on at once to § 198.

2. A CRYSTALLINE PRECIPITATE IS FORMED: presence of 168
MAGNESIA.* As testing for alkalies can proceed with certainty

* Phosphate of magnesia and ammonia is invariably crystalline; if phosphate of soda produces a slight flocculent precipitate, you are therefore not justified in concluding that magnesia is present. The slight flocculent precipitate, which is here

only after the removal of magnesia, evaporate the remainder of the fluid to dryness, and ignite until all ammoniacal salts are removed. Warm the residue with some water, add baryta-water (prepared from the crystals)* as long as a precipitate continues to form, boil, filter, add to the filtrate a mixture of carbonate of ammonia with ammonia in slight excess, heat for some time gently, filter, evaporate the filtrate to dryness, with addition of some chloride of ammonium (to convert into chlorides the caustic alkalies or alkaline carbonates that may happen to form), ignite gently, dissolve in a little water, precipitate if necessary once more with ammonia and carbonate of ammonia, filter, evaporate again, and if a residue remains, ignite this gently, and examine it according to § 197.

## § 197.

### (*Examination for Potassa and Soda.*)

YOU HAVE NOW TO EXAMINE FOR POTASSA AND SODA THE GENTLY IGNITED RESIDUE, FREE FROM SALTS OF AMMONIA AND ALKALINE EARTHS, WHICH HAS BEEN OBTAINED IN 167 OR 168. Dissolve it in a little water, filter if necessary, evaporate until there is only a small quantity of fluid left, and transfer one-half of this to a watch-glass, leaving the other half in the porcelain dish.

1. To the one-half in the porcelain dish add, after cooling, 169 a few drops of *bichloride of platinum*. If a yellow crystalline precipitate forms immediately, or after some time, POTASSA is present. Should no precipitate form, evaporate to dryness at a gentle heat, and treat the residue with a very small quantity of water, or, if chlorides alone are present, with a mixture of water and alcohol, when the presence of minute traces of potassa will be revealed by a small quantity of a heavy yellow powder being left undissolved (§ 89, 3). In the presence of an iodide the deep brown color of the fluid interferes with the detection of potassa by bichloride of platinum; under these circumstances test with acid tartrate of soda instead.

2. To the other half of the fluid (in the watch-glass) add some 170 *antimonate of potassa*. If this produces at once or after some time a crystalline precipitate, SODA is present. If, after standing twelve hours, no crystals separate, you may conclude that soda is absent. In regard to the crystalline form of the precipitate, and the precautionary rules, see § 90, 2.

sometimes obtained, consists of phosphate of alumina. You get it when alumina is contained in the original substance, and you use too large an excess of ammonia in precipitating the third and fourth groups. Its production depends upon the fact that phosphate of alumina is far less soluble in ammonia than the hydrate. Phosphate of alumina differs also from phosphate of ammonia and magnesia by its insolubility in acetic acid. If you want to test the precipitate in this manner, it should first be filtered off. From the acetic acid solution of phosphate of magnesia and ammonia, ammonia would throw down the pure salt.

* Or thin milk of lime, freed from every trace of alkali by repeated extraction with water. Add it to the warm fluid with stirring till turmeric-paper is strongly affected.

§ 198.

(*Examination for Ammonia.*)

THERE REMAINS STILL THE EXAMINATION FOR AMMONIA. 171
Triturate some of the substance with an excess of hydrate of lime, and, if necessary, a little water. If the escaping gas smells of ammonia, if it blues moist red litmus-paper, and forms white fumes with hydrochloric acid vapours, brought into contact with it by means of a glass rod, AMMONIA is present. The reaction is the most sensitive if the trituration is made in a small beaker, and the latter covered with a glass plate with a slip of moist turmeric or red litmus-paper adhering to the under-side.

*Complex Compounds.*

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.*

I. *In the Absence of Organic Acids.*

§ 199.

Consider, in the first place, which are the acids that form with the bases found compounds soluble in water, and let this guide you in the examination. To students the table given in Appendix IV. will prove of considerable assistance. The following plan of examination works best when the acids are combined exclusively with alkalies or alkaline earths, it is therefore sometimes advisable to precipitate any heavy metals present by sulphuretted hydrogen or sulphide of ammonium before proceeding. The sulphides should be filtered off and the excess of sulphuretted hydrogen removed by boiling, or of sulphide of ammonium by acidifying with hydrochloric acid, boiling and filtering off the sulphur. It must not be forgotten that sulphur, hydrochloric acid, chromic acid and chloric acid cannot be looked for in this fluid, and also that the results of the testing for sulphuric and nitric acids will not be so trustworthy.

1. THE ACIDS OF ARSENIC, CARBONIC ACID, SULPHUR com- 172
bined with metals or hydrogen, CHROMIC ACID, and SILICIC ACID will have been usually detected in the examination for bases, see **20, 67, & 68.** Chromic acid is also easily recognised by the yellow or reddish yellow color of the solution. If in doubt, test for it with acetate of lead and acetic acid (§ 138, 8) or—for very minute quantities—with decoction of logwood (§ 138, 12).

2. Add to a portion of the solution chloride of barium or, if lead, silver, or suboxide of mercury are present, nitrate of baryta, and, should the reaction of the fluid be acid, add ammonia to neutral or slightly alkaline reaction.

*a.* NO PRECIPITATE IS FORMED: absence of sulphuric 173
acid, phosphoric acid, chromic acid, silicic acid, oxalic acid,

* Consult also the explanations in the Third Section.

arsenious and arsenic acids, as well as of notable quantities of boracic acid and hydrofluoric acid.* Pass on to **175**.

*b.* A PRECIPITATE IS FORMED. Dilute the fluid, and add hydrochloric acid or, as the case may be, nitric acid; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present. **174**

3. Add nitrate of silver to a portion of the solution. If this fails to produce a precipitate, test the reaction, and if acid, add to the fluid some dilute ammonia, taking care to add the reagent so gently and cautiously that the two fluids do not intermix; if the reaction is alkaline, on the other hand, add with the same care some dilute nitric acid instead of ammonia, and watch attentively whether a precipitate or a cloud will form at the junction of the two fluids. **175**

*a.* NO PRECIPITATE IS FORMED AT THE JUNCTION OF THE TWO FLUIDS, EITHER IMMEDIATELY OR AFTER SOME TIME. Pass on to **181**; there is neither chlorine, bromine, iodine, cyanogen,† ferro- and ferricyanogen, nor sulphur present; nor phosphoric acid, arsenic acid, arsenious acid, chromic acid, silicic acid, oxalic acid; nor boracic acid, if the solution was not too dilute. **176**

*b.* A PRECIPITATE IS FORMED. Observe the colour‡ of it, then add nitric acid, and shake the mixture. **177**

*α. The precipitate dissolves completely:* absence of chlorine, bromine, iodine, cyanogen, ferro- and ferricyanogen, and also of sulphur. Pass on to **181**.

*β. A residue is left:* chlorine, bromine, iodine, cyanogen, ferro- or ferricyanogen may be present; and if the residue is black or blackish, HYDROSULPHURIC ACID or a soluble METALLIC SULPHIDE. The presence of sulphur may, if necessary, be readily confirmed, by mixing another portion of the solution with sulphate of copper, or with a solution of oxide of lead in soda. **178**

*aa.* Test another portion of the fluid for IODINE and subsequently for BROMINE, by the methods described in § 157.

*bb.* Test a small portion of the fluid with sesquichloride of iron for FERROCYANOGEN; and, if the color of the silver precipitate leads you to suspect the presence of FERRICYANOGEN, test another portion for this latter substance with sulphate of iron (freshly prepared, by warming wire with dilute sulphuric acid). If the original solution has an alkaline reaction, some hydrochloric acid must be added before the addition of the sesquichloride of iron, or of the sulphate of iron. **179**

* If the solution contains an ammoniacal salt in somewhat considerable proportion, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of these acids, since the baryta salts of most of them (not the sulphate) are in presence of ammoniacal salts more or less soluble in water.

† That the cyanogen in cyanide of mercury is not indicated by nitrate of silver has been mentioned (73).

‡ Chloride, bromide, cyanide, ferrocyanide, oxalate, silicate, and borate of silver are white; iodide, tribasic phosphate, and arsenite of silver are yellow; arsenate and ferricyanide of silver are browniah-red; chromate of silver is purple-red; sulphide of silver black.

*cc.* CYANOGEN, if present in form of a simple cyanide of an alkali metal soluble in water, may usually be readily recognised by the smell of hydrocyanic acid which the substance emits, and which is rendered more strongly preceptible by addition of a little dilute sulphuric acid. If ferrocyanogen and ferricyanogen are absent, cyanogen may be detected by the method given in § 155, 6. If they are present see § 226.

*dd.* Should bromine, iodine, cyanogen, ferrocyanogen, 180
ferricyanogen, and sulphur not be present, the precipitate which nitric acid has failed to dissolve consists of CHLORIDE of silver.

But where one or other of these bodies is present, a special examination for chlorine may become necessary, particularly when the quantity of the precipitate does not afford a decided indication.* See § 157.

4. CHLORIC ACID is known by the yellow color produced 181
when a little of the solid substance is brought into contact with concentrated sulphuric acid in a watch glass (§ 160).

5. NITRIC ACID is tested for with sulphate of iron and sulphuric acid (§ 159). The presence of certain other acids (chloric, chromic, hydriodic) impedes this reaction. If such acids are present they must be destroyed or removed. Chloric acid is destroyed by ignition (§ 161, at the end), chromic acid is reduced by sulphurous acid, the sesquioxide of chromium being precipitated afterwards with ammonia; hydriodic acid is removed by sulphate of silver.

You have still to test for phosphoric acid, boracic acid, silicic acid and oxalic acid, as well as for hydrofluoric acid.

For the first four acids test only in cases where both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. Compare also foot note to 173.

6. Test for PHOSPHORIC ACID, by adding to a portion of the 182
fluid ammonia in excess, then chloride of ammonium and sulphate of magnesia (§ 142, 7). Very minute quantities of phosphoric acid are detected most readily by means of molybdic acid (§ 142, 10). Arsenic acid, if present, must be first separated by sulphuretted hydrogen, the solution being acidified and kept at 70° during the passage of the gas.

7. To detect OXALIC ACID and HYDROFLUORIC ACID, add chloride of calcium to a fresh portion of the solution. If the reaction of the fluid is acid, add ammonia to alkaline reaction. If the chloride of calcium produces a precipitate which is not redissolved by addition of acetic acid, one or both bodies are present. Examine now a sample of the original substance for fluorine according to § 146, 5, another sample for oxalic acid according to § 145, 7.

8. Acidulate a portion of the fluid slightly with hydrochloric 183
acid, then test for BORACIC ACID, by means of turmeric paper (§ 144, 6). Chloric, chromic, and hydriodic acids impede the reaction. If present, they must be removed or destroyed as directed 181.

* Supposing, for instance, the solution of nitrate of silver to have produced a copious precipitate insoluble in nitric acid, and the subsequent examination to have shown mere traces of iodine and bromine, the presence of chlorine may be held to be demonstrated, without requiring additional proof.

9. Should SILICIC ACID not yet have been found in the course of testing for the bases, acidulate a portion of the fluid with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid (§ 150, 2).

*Complex Compounds.*

## A, 1. SUBSTANCES SOLUBLE IN WATER.

### DETECTION OF ACIDS.

### II. *In Presence of Organic Acids.*

### § 200.

1. The examination for the INORGANIC ACIDS, including oxalic acid, is made in the manner described § 199. As the tartrates and citrates of baryta and silver are insoluble, or at least difficultly soluble in water, tartaric acid and citric acid can be present only in cases where both chloride of barium and nitrate of silver have produced precipitates in the neutral fluid; still, in drawing a conclusion, you must bear in mind that these salts are slightly soluble in solutions of salts of ammonia. **184**

Before you commence testing for the ORGANIC ACIDS, you must remove all the bases of Groups III.—VI., as described in the beginning of § 184, since they might interfere.

2. Make a portion of the fluid feebly alkaline with ammonia, add some chloride of ammonium, then a sufficient quantity of chloride of calcium, shake vigorously, and let the mixture stand from ten to twenty minutes. **185**

*a.* NO PRECIPITATE IS FORMED, EVEN AFTER THE LAPSE OF SOME TIME. Absence of tartaric acid; pass on to **186**.

*b.* A PRECIPITATE IS FORMED, IMMEDIATELY, OR AFTER SOME TIME. Filter, and keep the filtrate for further examination according to **186**. Wash the precipitate, digest and shake it with solution of soda, without applying heat, then dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID is indicated. Filter hot, and test the precipitate with ammonia and nitrate of silver (§ 163, 8).

3. Mix the fluid in which chloride of calcium has failed to produce a precipitate, or that which has been filtered from the precipitate formed—in which latter case some more chloride of calcium is to be added—with 3 measures of alcohol. **186**

*a.* NO PRECIPITATE IS FORMED. Absence of citric, malic and succinic acids. Pass on to **190**. **187**

*b.* A PRECIPITATE IS FORMED. Filter and treat the filtrate as directed **190**. Treat the precipitate as follows:— **188**

Wash with alcohol, dissolve on the filter in a little dilute hydrochloric acid, add ammonia to the filtrate to alkaline reaction, and boil for some time.

*a.* IT REMAINS CLEAR. Absence of citric acid. Add more alcohol, filter off the precipitate, which may contain malate and succinate of lime, wash it a little with alcohol, dissolve in a porcelain dish, in a sufficient quantity of

strong nitric acid, and evaporate to dryness on the water-bath. Succinic acid will remain unchanged, malic acid is converted into oxalic acid with evolution of carbonic acid. Boil the residue with excess of solution of carbonate of soda, filter, neutralize exactly with hydrochloric acid, heat to remove carbonic acid, and mix a small portion of the fluid with solution of sulphate of lime. If a white precipitate is formed of oxalate of lime, MALIC ACID is indicated. If malic acid is indicated prepare some more of the lime precipitate, and confirm by testing it according to § 166; also test for succinic acid by mixing the rest of the fluid with excess of chloride of calcium, filtering, and adding alcohol to the filtrate; a precipitate indicates SUCCINIC ACID. If malic acid has not been found, test the rest of the neutralized fluid for SUCCINIC ACID with sesquichloride of iron (§ 168).

*β.* A HEAVY WHITE PRECIPITATE IS FORMED. Pre- 189
sence of CITRIC ACID. Filter boiling, and test the filtrate for malic and succinic acids as in *a*. To remove all doubt whether the precipitate is citrate of lime, redissolve it in hydrochloric acid, heat, supersaturate again with ammonia, and boil; the precipitate will now be thrown down again. (Compare § 164, 3.)

4. Heat the filtrate of **188**, or the fluid in which addition of 190
alcohol has failed to produce a precipitate (**187**), to expel the alcohol, neutralize *exactly* with hydrochloric acid, and add sesquichloride of iron. If this fails to produce a light brown flocculent precipitate, benzoic acid is absent. If a precipitate of the kind is formed, filter, and heat the washed precipitate with ammonia in excess; filter, evaporate the filtrate nearly to dryness, and test for BENZOIC ACID with hydrochloric acid (§ 169, 2). Benzoic acid may generally be readily detected in the original substance, by treating a small portion with dilute hydrochloric acid, which will leave the benzoic acid undissolved; it is then filtered off and heated on platinum foil (§ 169, 1).

5. Evaporate a portion of the solution to dryness—if acid, 191
after previous saturation with soda—introduce the residue or a portion of the original dry substance into a test tube, pour some alcohol over it, add about an equal volume of concentrated sulphuric acid, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of ACETIC ACID. This odor is rendered more distinctly perceptible by shaking the cooling or cold mixture.

6. Test for FORMIC ACID by just acidifying a portion with 192
hydrochloric acid (if not acid already), adding chloride of mercury and heating. A white turbidity from the separation of subchloride of mercury indicates formic acid (§ 172, 6). Confirm by nitrate of silver and by nitrate of suboxide of mercury (§ 172).*

* In the presence of chromic or chloric acid the reduction of the silver and mercury does not take place. If chromic acid is present, mix the original solution with sulphuric acid, add excess of oxide of lead, and shake, filter, mix the filtrate with excess of dilute sulphuric acid and distil. Test the distillate as above. If chloric acid is present, combine the acids with oxide of lead, and treat with alcohol; the

*Complex Compounds.*

## A, 2. Substances insoluble in Water, but soluble in Hydrochloric Acid, Nitric Acid, or Nitro-hydrochloric Acid.

### DETECTION OF THE ACIDS.

### I. *In Absence of Organic Acids.*

### § 201.

In the examination of these compounds attention must be directed to all acids, with the exception of chloric acid. Cyanogen compounds and silicates are not examined by this method. (Compare § 204 and § 205.)

1. Carbonic acid, sulphur (in the form of metallic sul- 193
phides), arsenious acid, arsenic acid and chromic acid, if present, have been found already in the examination for bases; nitric acid, if present, has been detected in the preliminary examination, by the ignition in a glass tube (8).

2. Mix a sample of the substance with 4 parts of pure carbon- 194
ate of soda and potassa, and, should a metallic sulphide be present, add some nitrate of soda; fuse the mixture in a platinum crucible if there are no reducible metallic oxides present, in a porcelain crucible if such oxides are present; boil the fused mass with water, and add a little nitric acid, leaving the reaction of the fluid, however, still alkaline; heat again, filter, and proceed with the filtrate according to § 199.*

3. As the phosphates of the alkaline earths are only incom- 195
pletely decomposed by fusion with carbonate of soda and potassa, it is always advisable in cases where alkaline earths are present, and phosphoric acid has not yet been detected, to dissolve a fresh sample of the substance in nitric acid, and test for phosphoric acid with solution of molybdic acid (§ 142, 10). In the presence of silicic or arsenic acid, prepare a solution with hydrochloric acid, separate these acids, add nitric acid, evaporate nearly to dryness, dilute with water containing nitric acid and then test with molybdate of ammonia.

4. If in the examination for bases, alkaline earths have been found, it is also advisable to test a separate portion for fluorine, by § 146, 5.

5. That portion of the substance which has been treated as 196
directed in 194, can be tested for silicic acid only in cases where the fusion has been effected in a platinum crucible; when a porcelain crucible has been used, examine a separate portion by evaporating the hydrochloric or nitric acid solution (§ 150, 3).

6. Examine a separate portion of the substance for oxalic acid by boiling with carbonate of soda, see 198. Acidify the alka-

formate is insoluble, the chlorate soluble. If tartaric acid is present it will also be safer to mix the fluid with dilute sulphuric acid and distil off the formic acid.

* In the presence of a metallic sulphide, a separate portion of it must be examined for sulphuric acid, by heating it with hydrochloric acid, filtering, diluting the filtrate, and adding chloride of barium.

line filtrate with acetic acid and test with solution of sulphate of lime. If a pulverulent precipitate is formed, this indicates oxalic acid. Confirm by taking a fresh portion of the substance, removing carbonic acid if necessary by dilute sulphuric acid, and then testing according to § 145, 7.

*Complex Compounds.*

A, 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

II. *In Presence of Organic Acids.*

§ 202.

1. Conduct the examination for INORGANIC ACIDS according to § 201. 197

2. Test for ACETIC ACID as directed § 171, 7.

3. To a small portion of the substance in a watch glass add a little dilute hydrochloric acid. If a residue remains, this should be tested for BENZOIC ACID by heating. Any considerable quantity of this acid is most readily detected in this way, but a small quantity might completely dissolve, it is therefore necessary to recur to this acid in 198.

4. Boil a portion of the substance for a few minutes with a large excess of solution of carbonate of soda, adding some of the solid if the solution is not strong, and filter. You will now have all the organic acids in the filtrate as soda salts. Evaporate the filtrate to concentrate it, acidify with hydrochloric acid, heat to drive off carbonic acid and proceed according to 185. If any heavy metals have passed into solution through the agency of organic acids, these must first be removed by hydrosulphuric acid or sulphide of ammonium. 198

*Complex Compounds.*

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID AND NITRO-HYDROCHLORIC ACID.

DETECTION OF THE BASES, ACIDS, AND NON-METALLIC ELEMENTS.

§ 203.*

To this class belong the following bodies. 199

SULPHATE OF BARYTA, SULPHATE OF STRONTIA, and SULPHATE OF LIME.†

SULPHATE OF LEAD‡ and CHLORIDE OF LEAD.§

* Compare the notes in the Third Section.

† Sulphate of lime passes partially into the solution effected by water, and often completely into that effected by acids.

‡ Sulphate of lead may pass completely into the solution effected by acids.

§ Chloride of lead can here only be found if the precipitate insoluble in acids has *not been thoroughly* washed with hot water.

CHLORIDE OF SILVER, bromide of silver, iodide of silver, cyanide of silver,* ferro- and ferricyanide of silver.†

SILICIC ACID and many SILICATES.

Native and ignited ALUMINA, and many aluminates.

Ignited sesquioxide of chromium and CHROMIC IRON (a compound of sesquioxide of chromium and protoxide of iron).

Ignited and native binoxide of tin (tin-stone).

Some metaphosphates and some arsenates.

FLUORIDE OF CALCIUM and a few other compounds of fluorine.

SULPHUR.

CARBONACEOUS MATTER.

Of these compounds those printed in small capitals are more frequently met with. As the silicates perform a highly important part in mineral analysis, a special chapter (§§ 205—208) is devoted to them.

The substance is in the first place subjected to the preliminary experiments described in *a*—*e*, unless the quantity at disposal is too small, when you at once pass on to **205**, bearing in mind, however, that the substance may contain all the aforesaid bodies.

*a*. Examine attentively the physical condition of the residue, **200** to ascertain whether it is homogeneous or not, whether it is sandy or pulverulent, whether it has the same colour throughout, or is made up of variously-colored particles, &c. A microscope, or even a lens, will be found very useful for this purpose.

*b*. Heat a small sample in a glass tube sealed at one end. If **201** brown fumes arise, and SULPHUR sublimes, this is of course a proof of the presence of that substance.

*c*. If the substance is black, this indicates, in most cases, the **202** presence of CARBONACEOUS MATTER (charcoal, coal, bone black, lamp black, graphite, &c.). Heat a small sample on platinum-foil over the blowpipe flame; if the black substance is consumed, it consisted of CARBON in some shape or other. Graphite (which may be readily recognised by its property of communicating its color to the fingers, to paper, &c.) requires the aid of oxygen for its combustion.

*d*. Heat a small sample, with a small lump of cyanide of potas- **203** sium and some water, for some time, filter, and test the filtrate with sulphide of ammonium. A brownish black precipitate indicates SILVER.

*e*. If an undissolved residue has been left in *d*, wash this **204** thoroughly with water, and if white, moisten it with sulphide of ammonium; if it turns black, salts of LEAD are present. If, however, the residue left in *d* is black, heat it with some acetate of ammonia, adding a few drops of acetic acid, filter, and test the filtrate for LEAD, by means of sulphuric acid and hydrosulphuric acid.‡

* Bromide, iodide, and cyanide of silver are decomposed by boiling with nitro-hydrochloric acid, and converted into chloride of silver; they can accordingly be found here only in cases where the operator has to deal with a substance which—as nitro-hydrochloric acid has failed to effect its solution—is examined directly by the method described here.

† With regard to the examination of these compounds, compare also § 204.

‡ The presence of lead in silicates, *e.g.* in glass, cannot be detected by this method.

The results obtained by these preliminary experiments serve as a guide in the following course.

1, *a*. SALTS OF LEAD ARE NOT PRESENT. Pass on to **206**. 205

*b*. SALTS OF LEAD ARE PRESENT. Heat the substance repeatedly with a concentrated solution of acetate of ammonia until the salt of lead is completely dissolved out. Test a portion of the filtrate for CHLORINE, another for SULPHURIC ACID, and the remainder for LEAD, by addition of sulphuric acid in excess, and by hydrosulphuric acid. If acetate of ammonia has left a residue, wash this, and treat it as directed in **206**.

2, *a*. SALTS OF SILVER ARE NOT PRESENT. Pass on to **207**. 206

*b*. SALTS OF SILVER ARE PRESENT. Digest the substance free from lead repeatedly with cyanide of potassium and water, at a gentle heat (in presence of sulphur, in the cold), until all the salt of silver is removed. If a *residue* is left, wash this, and proceed with it according to **207**. Of the *filtrate*, which contains cyanide of potassium, mix the larger portion with sulphide of ammonium, to precipitate the silver. Wash the precipitated sulphide of silver, then dissolve in nitric acid, dilute the solution, and add hydrochloric acid, to ascertain whether the precipitate really consisted of sulphide of silver. Test another small portion of the filtrate for SULPHURIC ACID.*

3, *a*. SULPHUR IS NOT PRESENT. Pass on to **208**. 207

*b*. SULPHUR IS PRESENT. Heat the substance free from silver and lead in a covered porcelain crucible until all the sulphur is expelled, and if a residue is left, treat this according to **208**.

4. Mix the substance free from silver, lead, and sulphur with 208
2 parts of carbonate of soda, 2 parts of carbonate of potassa, and 1 part of nitrate of potassa,† heat in a platinum crucible until the mass is in a state of calm fusion, place the red-hot crucible on a thick cold iron plate, and let it cool. By this means you will generally succeed in removing the fused mass from the crucible in a cake. Soak the mass now in water, boil, filter, and wash the residue until chloride of barium no longer produces a precipitate in the washings. (Add only the first washings to the filtrate.)

*a*. *The solution so obtained* contains the acids which were 209
present in the substance decomposed by fusing. But it may, besides these acids, contain also such bases as are soluble in caustic alkalies. Proceed as follows:—

*α*. Test a small portion for SULPHURIC ACID.

*β*. Test another portion (after acidifying with nitric acid)

* As the carbonate of potassa contained in the cyanide of potassium may have produced a total or partial decomposition of sulphates of the alkaline earths.

† Addition of nitrate of potassa is useful even in the case of white powders, as it counteracts the injurious action of silicate of lead, should any be present, upon the platinum crucible. In the case of black powders the proportion of nitrate of potassa must be correspondingly increased, in order that carbon, if present, may be consumed as completely as possible, and that any chromic iron present may be more thoroughly decomposed.

with molybdic acid for PHOSPHORIC ACID and ARSENIC ACID (§ 142, 10). If a yellow precipitate forms, test for arsenic acid with sulphuretted hydrogen and remove it by the same means if present, separate silicic acid if present, and then test again for phosphoric acid.

γ. Test another portion for FLUORINE (§ 146, 7).

δ. If the solution is yellow, CHROMIC ACID is presen . To confirm, acidify a portion of the solution with acetic acid, and test with acetate of lead.

ε. Acidify the remainder with hydrochloric acid, evapo- 210
rate to dryness, and treat the residue with hydrochloric acid and water. If a residue is left which refuses to dissolve even in boiling water, this consists of SILICIC ACID. Test the hydrochloric acid solution now in the usual way for those bases which, being soluble in caustic alkalies, may be present.

*b.* Dissolve *the residue left in* **208** in hydrochloric acid 211
(effervescence indicates the presence of alkaline earths—a residue insoluble in hydrochloric acid would have to be examined according to § 130, 8, as it might be BINOXIDE OF TIN), and test the solution for the bases as directed in § 190. (If much silicic acid has been found in **210**, it is advisable to evaporate the solution of the residue to dryness, and to treat with hydrochloric acid and water, in order that the silicic acid remaining may also be removed as completely as possible.)

5. If you have found in 4 that the residue insoluble in acids 212
contains a silicate, treat a separate portion of it according to **228**, to ascertain whether this silicate contains alkalies.

6. If a residue is still left undissolved upon treating the residue 213
left in **208** with hydrochloric acid (**211**), this may consist either of silicic acid which has separated, or of an undecomposed portion of sulphate of baryta; it may, however, also be fluoride of calcium, and if it is dark coloured, chromic iron, as the last-named two compounds are only with difficulty decomposed by the method given in **208**. As to fluoride of calcium, it may be easily decomposed by sulphuric acid. Chromic iron is best treated as follows :—Fuse 12 parts of bisulphate of potassa and project 1 part of the finely powdered mineral into the crucible, stir often and keep up the heat for half an hour, first gently, then raising it till the second equivalent of sulphuric acid is driven off. Add 6 parts of carbonate of soda, fuse, add gradually 6 parts of nitrate of potassa and after some time increase the heat, stirring diligently with a platinum wire. Finally allow to cool and boil with water.

7. If the residue insoluble in acids contained silver, you have 214
still to ascertain whether that metal was present in the original substance as chloride, bromide, iodide, &c., or whether it has been converted into the form of chloride by the treatment employed to effect the solution of the original substance. For that purpose treat a portion of the original substance with boiling water until the soluble part is completely removed; then treat the residuary portion in the same way with dilute nitric acid, wash the undissolved residue with water, and test a small sample of it for silver according to **203**. If silver is present, proceed to ascertain the salt.

radical with which the metal is combined; this may easily be effected by boiling the remainder of the residue with rather dilute solution of soda, filtering, and testing the filtrate, after acidifying it, for ferro- and ferricyanogen. Digest the washed residue now with finely granulated zinc and water, with addition of some sulphuric acid, and filter after the lapse of ten minutes. You may now at once test the filtrate for chlorine, bromine, iodine, and cyanogen; or you may first throw down the zinc with carbonate of soda, in order to obtain the salt-radicals in combination with sodium.

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# SECTION II.

## PRACTICAL COURSE IN PARTICULAR CASES.

### I. Analysis of Cyanides, Ferrocyanides, etc., insoluble in Water, and also of mixed Substances containing such Compounds.*

§ 204.

The analysis of ferrocyanides, ferricyanides, &c., by the common method is often attended by the manifestation of such anomalous reactions as easily to mislead the analyst. Moreover, acids often fail to effect the complete solution of these compounds. For these reasons it is advisable to analyze them, and mixtures containing them, by the following special method :— 215

1. Treat the substance with water until the soluble parts are entirely removed, and boil the residue with strong solution of potassa or soda; after a few minutes' ebullition add some carbonate of soda, and boil again for some time; filter, should a residue remain, and wash the latter.

*a. The residue* which is now free from cyanogen, (unless the substance contains cyanide of silver,) is examined by the common method, beginning at 35. 216

*b. The solution*, which, if combinations of compound cyanogen radicals (ferrocyanogen, cobalticyanogen, &c.), are present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by boiling with carbonate of soda, and lastly also, such oxides as are soluble in caustic alkalies. Treat it as follows— 217

*a.* Mix the alkaline fluid with hydrosulphuric acid, to test for metals of the fourth and fifth groups.† 218

*aa. No permanent precipitate is formed.* Absence of zinc and lead. Pass on to 219.

* Compare the notes in the Third Section.

† You must, of course, avoid adding solution of hydrosulphuric acid, or conducting hydrosulphuric acid gas into the fluid, until the mixture smells of the reagent (accordingly, until all the alkali present has been converted into hydrosulphate of sulphide of alkali metal), since this might lead to the precipitation also of the alumina which may be present in the alkaline solution, and even of sulphides of metals of the *sixth group*—a precipitation which is not intended here.

*bb. A permanent precipitate is formed.* Add to the fluid a little yellow sulphide of sodium, drop by drop, until the metals of the fourth and fifth groups present in the alkaline solution are just thrown down, heat moderately, filter, and treat the filtrate as directed **219**. Dissolve the washed precipitate in nitric acid, which may leave sulphide of mercury behind, and examine the solution for copper and lead, as well as for zinc and other metals of the fourth group, which may, in the same way as copper, have passed into the alkaline solution, by the agency of organic matters.

*β.* To test the alkaline fluid, which now also contains some **219** sulphide of an alkali metal, for mercury (which may be present, as its sulphide is soluble in sulphide of potassium) and for metals of the sixth group, mix with a sufficient quantity of water, then with dilute sulphuric acid to acid reaction, and if the fluid does not smell strongly of hydrosulphuric acid, add some more of the latter reagent.

*aa. No precipitate is formed.* Absence of mercury and the oxides of the sixth group. Pass on to **220**.

*bb. A precipitate is formed.* Filter, wash the precipitate, then examine it for mercury and the metals of the sixth group according to § 191.

*γ.* The fluid, acidified with sulphuric acid, may still con- **220** tain those metals which in combination with cyanogen form compound radicals (iron, cobalt, manganese, chromium), and, besides these, also alumina. You have to test it also for cyanogen, ferrocyanogen, cobalticyanogen, &c., and for other acids. Divide it therefore into two parts, *aa* and *bb*.

*aa.* Treat it according to § 199 or, as the case may be, § 200 to detect the acids.* (Cobalticyanogen may be recognised by giving a greenish precipitate with nickel salts and white precipitates with zinc and manganese salts, which may be proved to contain cobalt by means of the borax bead.)

*bb.* Evaporate it nearly to dryness, add some pure concentrated sulphuric acid and heat till the free acid is for the most part expelled. Dissolve the residue in water and test the solution for iron, manganese, cobalt, alumina, and sesquioxide of chromium according to § 194.

2. Decompose another portion by continued heating with pure concentrated sulphuric acid, remove all other bases and then test for alkalies.

## II. Analysis of Silicates.

### § 205.

Whether the substance is a silicate or contains one, is ascer- **221** tained by the preliminary examination with phosphate of soda and ammonia before the blowpipe; since in the process of fusion the

* It must be remembered that ferricyanogen may have been converted into ferrocyanogen by the oxidation of certain bases, &c., thus:—$Cy_6 Fe_2, 3K + KO, HO + 2FeO = 2(Cy_3 Fe, 2K) + Fe_2 O_3 + HO$.

metallic oxides dissolve, whilst the separated silicic acid floats about in the liquid bead as a translucent swollen mass (§ 150, 8).

The analysis of silicates differs, strictly speaking, from the common course only in so far as the preparatory treatment is concerned, which is required to separate the silicic acid from the bases, and to obtain the latter in solution.

The silicates and double silicates are divided into two classes, which require different methods of analysis; viz., (1) silicates readily decomposable by acids (hydrochloric acid, nitric acid, sulphuric acid), and (2) silicates which are not, or only with difficulty, decomposed by acids. Many rocks consist of mixtures of the two classes of silicates.

To ascertain to which class a given silicate belongs, reduce it to a very fine powder, and digest a portion with hydrochloric acid at a temperature near the boiling-point. If this fails to decompose it, try another portion by long-continued heating with a mixture of three parts of concentrated sulphuric acid and 1 part of water. If this also fails, the silicate belongs to the second class. Whether decomposition has been effected by the acid or not, may generally be learned from external indications, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely-pulverulent hydrate of silicic acid takes the place of the original heavy powder which grated under the glass rod with which it was stirred. But whether the decomposition is complete, or extends only to one of the components of the rock, may be ascertained by boiling the separated hydrate of silicic acid, after washing, in a solution of carbonate of soda. If perfect solution ensues, complete decomposition has been effected; if not, the decomposition is only partial. The results of these preliminary tests will show whether the silicate should be examined according to § 206, or § 207, or § 208.

Before proceeding further, examine a portion of the substance also for water, by heating it in a glass tube. If the substance contains hygroscopic moisture, it must first be dried at 100° for a long time. Apply a gentle heat at first, but ultimately an intense heat; you may also conveniently combine with this a preliminary examination for fluorine (§ 146, 8).

## A. Silicates decomposable by Acids.

### § 206.

*a. Silicates decomposable by hydrochloric or nitric acid.**

222 1. Digest the finely pulverized silicate with hydrochloric acid at a temperature near the boiling-point, until complete decomposition is effected, filter off a small portion of the fluid, evaporate the remainder, together with the silicic acid suspended therein, to dryness, heat the residue at 100° (scarcely above) with constant stirring, until hardly any more hydrochloric acid fumes escape, allow to cool, moisten with hydrochloric acid or, as the case may be, with nitric acid, afterwards add a little water, and heat gently for some time.

* Nitric acid is preferable to hydrochloric acid where compounds of silver or lead are present.

This operation effects the separation of the SILICIC ACID, and the solution of the bases in the form of chlorides or nitrates. Filter, wash the residue thoroughly, and examine the solution by the common method, beginning at § 189, II. or III. The residual silicic acid must always be tested, as it cannot under any circumstances be considered pure. It frequently contains titanic acid, occasionally sulphate of baryta, possibly also sulphate of strontia, and often a little alumina. It is best tested by repeated heating in a platinum dish with hydrofluoric and sulphuric acids, until all the silicic acid is removed in the form of fluoride of silicon. The residue is ignited, fused with bisulphate of potassa and then treated with cold water. If anything insoluble now remains, it is filtered off and tested according to § 99 for SULPHATE OF BARYTA (and strontia). The dilute aqueous solution is tested by long boiling for TITANIC ACID* (§ 104, 9), and the filtrate therefrom is tested by ammonia for ALUMINA. (Should there be any chance of the presence of chloride of silver in the silicic acid, digest a portion with ammonia, filter and examine the filtrate by supersaturation with nitric acid.)

2. As in silicates, and more particularly in those decomposed 223
by hydrochloric acid, there are often found other acids, as well as metalloids, the following observations and instructions must be attended to, that none of these substances may be overlooked :—

α. CARBONATES are detected in the process of treating with hydrochloric acid. SULPHIDES are often detected in the same operation, otherwise they are tested for according to § 156, 8.

β. If the separated silicic acid is black, and turns white upon ignition in the air, this indicates the presence of CARBON or of ORGANIC SUBSTANCES. In presence of the latter, the silicates emit an empyreumatic odor upon being heated in the glass tube.

γ. Test the portion of the hydrochloric acid solution filtered off before evaporating for SULPHURIC ACID, PHOSPHORIC ACID, and ARSENIC ACID—for sulphuric acid by diluting and adding chloride of barium; for arsenic acid by heating the solution to 70° and conducting sulphuretted hydrogen into it; for phosphoric acid by adding nitric acid, evaporating to dryness on the water-bath, warming the residue with nitric acid, filtering and adding molybdate of ammonia. Where arsenic is found, phosphoric acid is tested for in the fluid filtered from the sulphide of arsenic.

δ. BORACIC ACID is best detected by fusing a portion of 224
the substance in a platinum spoon with carbonate of soda and

* If the silicic acid has been separated by evaporation on the water-bath, only a small part of the titanic acid will be found remaining with it, the rest will pass into the hydrochloric acid solution and will be precipitated by ammonia in conjunction with the sesquioxide of iron and alumina. To find this, fuse the dried precipitate with bisulphate of potassa, dissolve the fusion in cold water, filter if necessary, dilute considerably, pass sulphuretted hydrogen until all the sesquioxide of iron is reduced, and (without filtering off the sulphur) keep the fluid boiling for half an hour with a constant current of carbonic acid passing through it. Filter, wash and ignite; the sulphur will burn off, the titanic acid will remain. Should it still contain iron, redissolve it by fusion with bisulphate of potassa and treatment with cold water, and precipitate by boiling with hyposulphite of soda.

potassa, boiling the fused mass with water, and testing the solution by § 144, 6.

ε. With many silicates, boiling with water is sufficient to dissolve the CHLORIDES present, which may then be readily detected in the filtrate by nitrate of silver; the safest way, however, is to dissolve the mineral in dilute nitric acid, and test the solution with nitrate of silver.

ζ. FLUORIDES, which often occur in silicates in greater or smaller proportion, are detected by § 146, 6.

*b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.*

225 Heat the finely pulverized mineral with a mixture of 3 parts of concentrated pure sulphuric acid and 1 part of water (best in a platinum dish), finally drive off the greater portion of the sulphuric acid, boil the residue with hydrochloric acid, dilute, filter, and treat the filtrate as directed § 190; and the residue, which, besides the separated silicic acid, may contain also sulphates of the alkaline earths, &c., as directed § 206, 1. If you wish to examine silicates of this class for acids and salt radicals, treat a separate portion of the substance according to § 207.

## B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.*

### § 207.

226 As the silicates of this class are most conveniently decomposed by fusion with carbonate of soda and potassa, the portion so treated cannot, of course, be examined for alkalies. The analytical process is therefore divided into two principal parts, a portion of the mineral being examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter. The mineral must also be examined for other acids.

1. *Detection of the silicic acid and the bases, with the exception of the alkalies.*

227 Reduce the mineral to a very fine powder, mix this with 4 parts of carbonate of soda and potassa, and heat the mixture in a platinum crucible over a gas or Berzelius spirit-lamp until the mass is in a state of calm fusion. Place the red-hot crucible on a thick cold iron plate, and let it cool there: this will generally enable you to remove the fused cake from the crucible, in which case break the mass to pieces, and keep a portion for the examination for acids. Put the remainder, or, if the mass still adheres to the crucible, the latter with its contents into a porcelain dish, pour water over it, add hydrochloric acid, and heat gently until the mass is dissolved, with the exception of the silicic acid, which

* It will be understood, from what has been stated § 205, that these are not decomposed by heating with hydrochloric acid and sulphuric acid in open vessels; but by heating them, reduced to a fine powder, in a sealed glass tube, with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water, or with hydrochloric acid, to 200°—210°, most of them are decomposed, and may accordingly be analyzed also in this manner (AL. MITSCHERLICH).

separates in flakes. Remove the crucible from the dish if necessary, evaporate to dryness, and treat the residue as directed **222**.

2. *Detection of the alkalies.*

To effect this the silicate must be decomposed by means of **228** a substance free from alkalies. Hydrofluoric acid or a metallic fluoride answers this purpose best; but fusion with hydrate of baryta will also answer the purpose.

*a.* DECOMPOSITION BY MEANS OF A METALLIC FLUORIDE.—Mix 1 part of the very finely pulverized mineral with 5 parts of fluoride of barium, or pure, finely pulverized fluoride of calcium, or with 3 parts of fluoride of ammonium, stir the mixture in a platinum crucible with concentrated sulphuric acid to a thickish paste, and heat gently for some time in a place where the fumes will be well carried away; finally heat a little more strongly, until the excess of sulphuric acid is completely expelled. Boil the residue with water, add chloride of barium cautiously as long as a precipitate continues to form, then baryta-water to alkaline reaction, boil, filter, mix with carbonate of ammonia and some ammonia as long as a precipitate forms, and proceed as directed **168**.

*b.* DECOMPOSITION BY MEANS OF HYDRATE OF BARYTA.— **229** Mix 1 part of the very finely pulverized substance with 4 parts of hydrate of baryta, expose the mixture for half an hour in a platinum crucible to the strongest possible heat of a good Berzelius or gas-lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until all the bases are dissolved; precipitate with ammonia and carbonate of ammonia, filter, evaporate to dryness, ignite, dissolve the residue in water, add a little pure lime, boil, filter, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite, and test the residue for potassa and soda as directed § 197.

3. *Examination for fluorine, chlorine, boracic acid, phosphoric acid, arsenic acid, and sulphuric acid.*

Use for this purpose the portion of the fused mass reserved in **230** **227**, or, if necessary, fuse a separate portion of the finely pulverized substance with 4 parts of pure carbonate of soda and potassa until the mass flows calmly; boil the fused mass with water, filter the solution, which contains all the fluorine as fluoride of sodium, all the chlorine as chloride of sodium, all the boracic acid as borate, all the sulphuric acid as sulphate, all the arsenic acid as arsenate, and at least part of the phosphoric acid as phosphate of soda, and treat as follows:—

*a.* Acidify a small portion with nitric acid, and test for CHLORINE with nitrate of silver.

*b.* Test another portion for BORACIC ACID as directed § 144, 6.

*c.* To detect FLUORINE, treat a third portion as directed § 146, 7.

*d.* Acidify the remainder with hydrochloric acid and test a small portion with chloride of barium for SULPHURIC ACID; heat the remainder to 70°, and test with hydrosulphuric acid

for ARSENIC ACID. If no precipitate forms, evaporate the fluid, if a precipitate forms, the filtrate, with addition of nitric acid, to dryness, treat the residue with nitric acid and water, and examine the solution for PHOSPHORIC ACID with sulphate of magnesia, or with molybdate of ammonia (§ 142).

### C. SILICATES WHICH ARE PARTIALLY DECOMPOSED BY ACIDS.

§ 208.

231 Most rocks are mixtures of several silicates, of which some are often decomposable by acids, others not. If such substances were analyzed by the same method as the absolutely insoluble silicates, the analyst would indeed detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the mineral.

It is therefore advisable to examine separately those constituents which show a different deportment with acids. For this purpose digest the very finely pulverized substance for some time with hydrochloric acid at a gentle heat, filter off a small portion of the solution, evaporate the remainder with the residue to dryness, heat the residue at 100° (scarcely above), with stirring, until no more, or very little hydrochloric acid vapor is evolved, allow to cool, moisten with hydrochloric acid, heat gently with water, and filter.

The filtrate contains the bases of that part of the mixed mineral which has been decomposed by hydrochloric acid; examine this as directed **222**. Examine the portion first filtered off as directed **223**, $\gamma$. Test portions of the original substance for other acids as directed **223** $\alpha$ & $\beta$ and **224**. Boil the residue—which, besides the silicic acid separated from the decomposed portion of the silicate, contains that part of the mixed mineral which has resisted the action of the hydrochloric acid—with an excess of solution of carbonate of soda, filter hot, and wash, first with hot solution of carbonate of soda, finally with boiling water. Treat the residuary undecomposed part of the mineral, thus freed from the admixed separated silicic acid, according to § 207. Acidify the alkaline filtrate with hydrochloric acid, evaporate to dryness, treat with hydrochloric acid and water, filter off the silicic acid, render the filtrate alkaline with ammonia and warm; the precipitate thus formed (if any) is to be treated with the separated silicic acid according to **222**, in order to detect titanic acid. In cases where it is of no interest to effect the separation of the silicic acid of the part decomposed by acids, you may omit the troublesome operation with carbonate of soda, and may proceed at once to the decomposition of the residue.

## III. ANALYSIS OF NATURAL WATERS.

§ 209.

232 In the examination of natural waters the analytical process is simplified by the circumstance that we know from experience what substances are usually present. Now, although a quantitative

analysis alone can properly inform us of the true character of a water, since the differences between waters are principally caused by the different proportions of the constituents; still a qualitative analysis may render very good service, especially if the analyst notes whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate; since these circumstances will enable him to make an approximate estimation of the relative proportions of the constituents.

I separate here the analysis of ordinary drinking waters from that of mineral waters, in which latter we may also include sea-water; for, although no well-defined line can be drawn between the two classes, still the analytical examination of the former is necessarily by far the simpler, as the number of substances to be looked for is much more limited.

## A. Analysis of Potable Waters (Spring-water, Well-water, River-water, &c.)

### § 210.

We know from experience that the substances to be had regard 233
to in the analysis of such waters are the following:—

*a.* Bases: Potassa, soda, ammonia, lime, magnesia, protoxide of iron.

*b.* Acids, &c.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, nitrous acid, chlorine.

*c.* Organic matter.

*d.* Mechanically suspended substances: Clay, &c.

Potable waters contain indeed also other constituents besides those enumerated here, as may be inferred from the origin and formation of springs, &c., and as has, moreover, been fully established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they escape detection, unless hundreds of pounds of the water are subjected to the analytical process. I therefore omit here the mode of their detection (see § 211).

1. Boil 1000 to 2000 grm. of the carefully collected water in 234
a porcelain dish to one half. (Glass vessels are to be avoided, as boiling water attacks them much more than porcelain.) This generally produces a precipitate. Pass the fluid through a perfectly clean filter (free from iron and lime), wash the precipitate well, after having removed the filtrate, then examine both as follows:

*a. Examination of the precipitate.*

The precipitate contains those constituents of the water 235
which were only kept in solution through the agency of free

* Chatin (Journ. de Pharm. et de Chim. (3), 27, 418) found iodine in all fresh-water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, &c., contains traces, even though extremely minute, of metallic iodides. According to Marchand (Comp. Rend., 31, 495), all natural waters contain iodine, bromine, and lithia. Van Ankum has demonstrated the presence of iodine in almost all the potable waters of Holland. And it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontia, baryta, fluorine, &c.

carbonic acid, or, as the case may be, in the form of bicarbonates, viz., carbonate of lime, carbonate of magnesia, sesquioxide of iron (which was in solution as bicarbonate of protoxide of iron, and precipitates upon boiling as hydrate, as silicate, and in presence of phosphoric acid, also as phosphate), phosphate of lime; also silicic acid, sometimes sulphate of lime (if that substance is present in large proportion) and clay which was mechanically suspended in the water.

Dissolve the precipitate on the filter in the least possible quantity of dilute hydrochloric acid (effervescence indicates CARBONIC ACID), and treat separate portions of the solution as follows:—

*a.* Add sulphocyanide of potassium, or ferrocyanide of potassium, drop by drop, to test for IRON.

*β.* Boil, add ammonia, filter if necessary, mix the 236
filtrate with excess of oxalate of ammonia, and let the mixture stand for some time in a warm place. A white precipitate indicates LIME (in the form of carbonate, or also in that of sulphate if sulphuric acid is detected in *γ*). Filter, mix the filtrate again with ammonia, add some phosphate of soda, stir with a glass rod, and let the mixture stand for twelve hours. A white crystalline precipitate, which is often visible only on the sides of the vessel when the fluid is poured out, indicates MAGNESIA (as carbonate).

*γ.* Add chloride of barium, and let the mixture stand for twelve hours in a warm place. A precipitate indicates SULPHURIC ACID. If very small it is best seen by cautiously decanting the supernatant clear fluid and shaking the small remaining quantity about in the glass.

*δ.* Evaporate with addition of nitric acid to dryness, 237
treat the residue with nitric acid and water, filter off any SILICIC ACID and test the filtrate for PHOSPHORIC ACID with molybdate of ammonia (§ 142, 10), or with acetate of soda and sesquichloride of iron (§ 142, 9).

*b. Examination of the filtrate.*

*a.* Mix a portion with a little hydrochloric acid and 238
chloride of barium. A white precipitate, which makes its appearance at once, or perhaps only after standing some time, indicates SULPHURIC ACID.

*β.* Mix a portion with nitric acid, and add nitrate of silver. A white precipitate or turbidity indicates CHLORINE.

*γ.* Test a portion for PHOSPHORIC ACID, by evaporating with nitric acid, taking up with the same and proceeding as in 237.

*δ.* Evaporate a large portion until highly concentrated, and test the reaction of the fluid. If it is alkaline, if a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, and if carbonate of lime precipitates on the cautious addition of chloride of calcium to the alkaline fluid, then a CARBONATE of an alkali is present. Should this be the case, evaporate the fluid to perfect dryness, boil the residue with spirit of wine, filter,

evaporate the solution to dryness, dissolve the residue in a little water, and test the solution for NITRIC ACID as directed § 159, 7, 8 or 9.*

*c.* Mix the remainder of the filtrate with chloride of ammonium, ammonia, and excess of oxalate of ammonia, and let the mixture stand some time. A precipitate indicates LIME. Filter, and—

*aa.* Test a small portion with ammonia and phosphate of soda for MAGNESIA.

*bb.* Evaporate the remainder to dryness, ignite, remove the magnesia which may be present (168), and test for POTASSA and SODA, according to § 197.

2. Acidify a tolerably large portion of the filtered water with pure hydrochloric acid, and evaporate nearly to dryness; divide the residue into two parts, *a* and *b*. 239

*a.* Test with hydrate of lime for AMMONIA (§ 91, 3).†

*b.* Evaporate to dryness, moisten the residue with hydrochloric acid, add water, warm, and filter if a residue remains. The residue may consist of SILICIC ACID and, if the water has not been filtered quite clear, also of CLAY; these two substances may be separated by boiling with solution of carbonate of soda. The residue is often dark-colored from the presence of organic substances; but it becomes perfectly white upon ignition.

3. Mix another portion of the water, freshly taken, with lime-water. If a precipitate is produced, FREE CARBONIC ACID or BICARBONATES are present. If free carbonic acid is present, no permanent precipitate is obtained when a large portion of the water is mixed with only a small amount of lime-water, since in that case soluble bicarbonate of lime is formed. 240

4. Test for NITROUS ACID,‡ by mixing a portion of the water with some iodide of potassium and starch paste (made of 1 part of the purest iodide of potassium, 20 parts of starch, and 500 parts of water) and pure dilute sulphuric acid, and observe whether a blue coloration makes its appearance, either at once or, at least, after a few minutes (§ 158, 1). The reagents should be tested by making a counter experiment with pure water. 241

5. ORGANIC MATTER is detected by the blackening which occurs when a portion of the water is evaporated to dryness and gently ignited. If this experiment is to give conclusive results, the evaporation as well as the ignition must be conducted in a flask or retort. 242

6. FETID SUBSTANCES (decaying organic matter) are detected best by filling a bottle two-thirds with the water, covering it with the hand, shaking, and smelling. If the smell is of sulphuretted hydrogen, proceed as directed § 212, 3. Whether there are other smelling organic matters present besides, may be ascertained

* The nitric acid may often be found without trouble, by evaporating the water to a small residue, and testing this at once for it.

† In clear water ammonia may be tested for quite satisfactorily without evaporating either by means of chloride of mercury and carbonate of potassa or by NESSLER'S test (§ 92).

‡ SCHÖNBEIN found this acid in rain- and snow-water.

by adding a little sulphate of copper to the water, before smelling it.

7. If you wish to examine the MATTERS MECHANICALLY SUSPENDED in a water (in muddy river-water, for instance) fill a large glass bottle with the water, cork securely, and let it stand at rest for several days, until the suspended matter has subsided; remove now the clear supernatant fluid with the aid of a syphon, filter the remainder, and examine the sediment remaining on the filter. As this sediment may consist of the finest dust of various minerals, treat it first with dilute hydrochloric acid, then examine the part insoluble in that menstruum as directed § 205. 243

8. As OXIDE OF LEAD may be present, arising from leaden pipes, treat a large quantity with sulphuretted hydrogen, allow to stand for some time, and should a black precipitate form, examine this as directed § 193. To detect very minute traces of lead, acidify 6 or 8 litres of the water with acetic acid, add a little acetate of ammonia, to prevent the lead precipitating as sulphate, evaporate to a small residue, filter, conduct hydrosulphuric acid into the filtrate, and examine a black precipitate which may form by § 193.

## B. Analysis of Mineral waters.

### § 211.

The analysis of mineral waters embraces a larger number of constituents than that of potable water. The following are the principal of the additional bodies to be looked for:— 244

OXIDE OF CÆSIUM, OXIDE OF RUBIDIUM, OXIDE OF THALLIUM, LITHIA, BARYTA, STRONTIA, ALUMINA, PROTOXIDE OF MANGANESE, BORACIC ACID, BROMINE, IODINE, FLUORINE, HYDROSULPHURIC ACID (hyposulphurous acid),* CRENIC ACID and APOCRENIC ACID, (formic acid, propionic acid, &c., nitrogen gas, oxygen gas, light carburetted hydrogen gas).*

The analyst has moreover to examine the muddy ochreous or hard sinter-deposits of the spring, or also the residue left upon the evaporation of very large quantities of water, for ARSENIOUS ACID, ARSENIC ACID, TEROXIDE OF ANTIMONY, OXIDE OF COPPER, OXIDE OF LEAD, PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, and the oxides of other heavy metals. The greatest care is required in this examination, to ascertain whether these oxides come really from the water, and do not perhaps proceed from metal pipes, stopcocks, &c.† The absolute purity of the reagents employed in these delicate investigations must also be ascertained with the greatest care.

* Respecting the constituents in brackets, I refer to the corresponding chapter in my Quantitative Analysis, as the detection of these matters generally comprises also their quantitative estimation.

† On the subject of water analysis, compare the following works by Dr. FRESENIUS:— Chemische Untersuchung der wichtigsten Nassauischen Mineralwasser. I. der Kochbrunnen zu Wiesbaden, II. die Mineralquellen zu Ems, III. die Quellen zu Schlangenbad, IV. die Quellen zu Langenschwalbach, V. die Schwefelquelle zu Weilbach, VI. die Mineralquelle zu Geilnau, VII. die neue Natronquelle zu Weilbach, VIII. die Mineralquelle zu Niederselters, IX. die Mineralquelle zu Fachingen; Wiesbaden: Kreidel, 1850—1868. Untersuchung der Mineralquellen zu Wildungen; Arolsen: Mittler, 1860. Analyse des Kaiser- und des Ludwigsbrunnens, wie der

## I. Examination of the Water.

### *a.* Operations at the Spring.

### § 212.

1. Filter the water, if not perfectly clear, through exhausted 245
filter paper, into large bottles with glass stoppers. The sediment remaining on the filter, which possibly contains, besides the flocculent matter suspended in the water, also those constituents which separate at once upon coming in contact with the air (hydrate of sesquioxide of iron, and compounds of sesquioxide of iron with phosphoric acid, silicic acid, arsenic acid), is taken to the laboratory, to be examined afterwards according to § 214.

2. The presence of FREE CARBONIC ACID is usually sufficiently 246
visible to the eye. However, to convince yourself by positive reactions, test the water with fresh-prepared solution of litmus, and with lime-water. If carbonic acid is present, the former acquires a wine-red color; the latter produces turbidity, which must disappear again upon addition of the mineral water in excess.

3. Free HYDROSULPHURIC ACID is most readily detected by the 247
smell. For this purpose half fill a bottle with the mineral water, cover with the hand, shake, and smell the bottle. In this way distinct traces of hydrosulphuric acid are often found which would escape detection by reagents. However, if you wish to have some visible reactions, fill a large white bottle with the water, add a few drops of solution of acetate of lead in soda, place the bottle on a white surface, and look in at the top, to see whether the water acquires a brownish color or deposits a blackish precipitate;—or half fill a large bottle with the water, and close with a cork to which is attached a slip of paper previously saturated with solution of acetate of lead and then moistened with carbonate of ammonia; shake the bottle gently from time to time, and observe whether the paper acquires a brownish tint in the course of a few hours. If the addition of the acetate of lead has produced a brown color, or precipitate, whilst the test with the paper gives no result, this indicates that the water contains an alkaline sulphide, but no free hydrosulphuric acid.

4. Mix a wineglassful of the water with some tannic acid, another 248
wineglassful with some gallic acid. If the former imparts a red-violet, the latter a blue-violet color, PROTOXIDE OF IRON is present. Instead of the two acids, you may employ infusion of galls, which contains them both. The colorations make their appearance only after some time, and increase in intensity from the top—where the air acts on the fluid—towards the bottom of the vessel.

5. Test for NITROUS ACID and FETID ORGANIC SUBSTANCES 249
according to 241 and 242. If the water contains hydrosulphuric

Elisabethenquelle zu Homburg v. d. H.; Wiesbaden: Kreidel, 1863 und 1864. Analyse der Trinkquelle, der Badequelle und der Helenenquelle zu Pyrmont; Arolsen: Speyer, 1865. Analyse der Driburger und Herster Quelle; Wiesbaden: Kreidel, 1866. Analyse der Augustaquelle (Felsenquelle Nr. II.) und der Victoriaquelle zu Bad Ems; Wiesbaden: Kreidel, 1866 und 1869. Analyse des Lamscheider Mineralbrunnens, sowie die des Tönnisteiner Heilbrunnens und des Tönnisteiner Stahlbrunnens, 1869.

acid, remove it before testing for nitrous acid by very cautious addition of sulphate of silver (no silver salt must under any circumstances remain in the solution).

### *b.* Operations in the Laboratory.

### § 213.

As it is always desirable to obtain even in the qualitative examination some information as to the proportions in which the several constituents are present, it is advisable to analyze a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the relative proportions in which these constituents exist, and thus to determine the character of the water; then to examine a far larger portion for the constituents which are present in small quantity; and finally a very large portion or the sinter for those constituents which are present merely in traces. For this purpose proceed as follows:—

1. Examination for those constituents which are present in large quantities.

250 *a.* Boil about 3 lbs. of the clear water, or of the water filtered at the spring, in a porcelain dish (a flask is less suitable) for one hour, taking care, however, to add from time to time some distilled water, that the quantity of liquid may remain undiminished, and thus that only those salts may be separated which owe their solution to the presence of carbonic acid. Filter and examine the precipitate and the filtrate as directed § 210.

*b.* Test for ammonia, silicic acid, organic matters, &c., by the methods given in § 210.

2. Examination for those fixed constituents which are present in minute quantities.

251 Evaporate a large quantity (at least 20 lbs.) of the water in a silver or porcelain dish to dryness; conduct this operation with the most scrupulous cleanliness in a place as free as possible from dust. If the water contains no carbonate of an alkali, add pure carbonate of potassa in slight excess. The process of evaporation may be conducted at first over a gas-lamp, but ultimately the sand-bath must be employed. Heat the dry mass to very faint redness; if in a silver dish, you may at once proceed to ignite it; but if you have it in a porcelain dish, first transfer it to a silver or platinum vessel before proceeding to ignition. If the mass turns black in this process, organic matters may be assumed to be present.*

Mix the residue thoroughly, and divide it into 3 portions, *a* and *b* being each about a quarter, and *c* one half.

*a.* Examination for phosphoric acid.

252 Warm the portion *a* with water, add pure nitric acid in sufficient excess, evaporate on the water-bath to dryness, warm

* This inference is, however, correct only if the water has been effectually protected from dust during evaporation; if this has not been the case, and you yet wish to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If you find organic matter, and wish to know whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed § 214, 3.

the residue with nitric acid, dilute slightly, filter through paper exhausted with hydrochloric acid and test with molybdate of ammonia (§ 142, 10).

*b.* EXAMINATION FOR FLUORINE.

Heat the portion *b* with water, add chloride of calcium as 253
long as a precipitate continues to form, let deposit and collect the precipitate, which consists chiefly of carbonates of lime and magnesia, on a filter. Wash, dry, ignite, treat with water in a small dish, add acetic acid in slight excess, evaporate on the water-bath to dryness, keeping the dish on the bath until all smell of acetic acid has disappeared, add water, heat, filter off the solution of the acetates of the alkaline earths, wash, dry or ignite the residue, and test it as directed § 146, 5.

*c.* EXAMINATION FOR THE REMAINING FIXED CONSTITUENTS PRESENT IN MINUTE QUANTITIES.

Boil the portion *c* repeatedly with water, filter, and wash 254
the undissolved residue with boiling water. You have now a residue ($\alpha$), and a solution ($\beta$).

*a.* The *residue* consists chiefly of carbonate of lime, carbonate of magnesia, silicic acid, and—in the case of chalybeate springs—hydrate of sesquioxide of iron. But it may contain also minute quantities of BARYTA, STRONTIA, ALUMINA, PEROXIDE OF MANGANESE, and TITANIC ACID, and must accordingly be examined for these substances.

Treat it with water in a platinum or porcelain dish, add hydrochloric acid to slightly acid reaction, then 4 or 5 drops of dilute sulphuric acid, evaporate on the water-bath to dryness, moisten with a small quantity of hydrochloric acid, then add water, warm gently, filter, and wash.

*aa.* EXAMINATION OF THE RESIDUE INSOLUBLE IN 255
HYDROCHLORIC ACID. This will mostly consist of silicic acid; but it may contain also sulphates of the alkaline earths, titanic acid and carbon. Heat it in a platinum dish repeatedly with hydrofluoric acid or fluoride of ammonium with addition of sulphuric acid, till all silicic acid is expelled. Finally evaporate to dryness, fuse the residue (if any) with bisulphate of potassa, treat the fusion with cold water, filter and test the solution for TITANIC ACID by protracted boiling. If there was a residue on treating the fusion with water, wash it and incinerate the filter. When a spectroscope is at disposal, take up the ash on the loop of a platinum wire, expose for some time to the reducing flame, moisten with hydrochloric acid and examine for BARYTA. Strontia will not be found here except perhaps in traces. When a spectroscope is not at hand, set aside the ash for subsequent examination.

*bb.* EXAMINATION OF THE HYDROCHLORIC ACID 256
SOLUTION. Mix in a flask with pure chloride of ammonium, add ammonia until the fluid is just alkaline, then sulphide of ammonium free from ammonia; close the flask, filled to the neck, and let it stand for 24 hours in a moderately warm place. If a precipitate has formed at the end of that time, filter off, dissolve in hydrochloric acid,

boil, add potassa (§ 34, *c*) in excess, boil again, filter, and test the *filtrate* for ALUMINA by acidifying with hydrochloric acid and heating with ammonia;* divide the *residue* into two parts, test one for MANGANESE with carbonate of soda before the blowpipe, the other for IRON by dissolving in hydrochloric acid and adding sulphocyanide or ferrocyanide of potassium.

The filtrate from the sulphide of ammonium precipitate may contain traces of baryta and will contain all or nearly all the strontia. Add to it carbonate of ammonia, filter after long standing, wash the precipitate, dry, subject it to ENGELBACH'S process (end of § 99), and treat the aqueous extract of the ignited precipitate as follows. If a spectroscope is at command, evaporate it to dryness with hydrochloric acid and examine the residue in the instrument. If a spectroscope is not at command, evaporate it nearly to dryness with sulphate of ammonia, boil with a saturated solution of sulphate of ammonia, filter, wash the precipitate, dry, incinerate, add the residue set aside in **255**, fuse with carbonate of soda, treat with water, wash, dissolve the residue in hydrochloric acid and test the solution according to § 99.

*β*. The *alkaline solution* contains the salts of the alkalies, **257** and usually also magnesia and traces of lime. You have to examine it now for NITRIC ACID,† BORACIC ACID, IODINE, BROMINE, and LITHIA. Evaporate until very concentrated, let it cool, and place the dish in a slanting position, that the small quantity of liquid may separate from the saline mass; transfer a few drops of the concentrated solution to a watch-glass by means of a glass rod, just acidify with hydrochloric acid, and test with turmeric-paper for BORACIC ACID. Evaporate the whole contents of the dish, with stirring, to perfect dryness, and divide the residuary powder into 2 portions, *aa* being about two-thirds, and *bb* one-third.

*aa*. EXAMINE THE LARGER PORTION FOR NITRIC **258** ACID, IODINE, AND BROMINE.

Put the powder into a flask, add alcohol of 90 per cent., boil in the water-bath, and filter hot; repeat the same operation a second and a third time. Mix the alcoholic extract with a few drops of potassa, distil almost all the spirit off, and allow to cool. If minute crystals separate these may consist of nitrate of potassa; pour off the fluid, wash the crystals with some spirit, dissolve in a very little water, and test the solution for NITRIC ACID, with indigo, or with brucia, or with iodide of potassium, starch-paste and zinc (§ 159). Evaporate the alcoholic solution

* There is no use in testing for alumina unless the evaporation has been effected in a platinum or silver dish.

† The nitric acid originally present may have been destroyed by the ignition of the residue in 251, if the latter contained organic matter. If you have reason to fear that such has been the case, and you have not already found nitric acid in 250, examine a larger portion of non-ignited residue for that acid, according to the directions of 258.

now to dryness. If you have not yet found nitric acid, dissolve a small portion of the residue in a very little water, and examine the solution for that acid. Treat the remainder or, as the case may be, the whole of the residue three times with warm alcohol, filter, evaporate the filtrate to dryness with addition of a drop of potassa, dissolve the residue in a very little water, acidify slightly with sulphuric acid, add some pure bisulphide of carbon, and test for IODINE with nitrite of potassa, or a drop of solution of hyponitric acid in sulphuric acid. After having carefully observed the reaction, test the same fluid for bromine with chlorine water according to § 157.

*bb.* EXAMINE THE SMALLER PORTION FOR LITHIA. 259
Warm the smaller portion of the residue (which, if lithia is present, must contain that alkali as carbonate or phosphate) with water, add hydrochloric acid to distinctly acid reaction, evaporate *nearly* to dryness, then mix with pure alcohol of 90 per cent., which will separate the greater portion of the chloride of sodium, and dissolve all the lithia. Drive off the alcohol by evaporation and, if you have a spectroscope, examine the residue with this for LITHIA (§ 93, 3). If you have no spectroscope, dissolve the residue in water and a few drops of hydrochloric acid, add a little sesquichloride of iron, then ammonia in *slight* excess, and a small quantity of oxalate of ammonia; let the mixture stand for some time, then filter off the fluid, which is now entirely free from phosphoric acid and lime; evaporate the filtrate to dryness, and gently ignite until the salts of ammonia are expelled; treat the residue with some chlorine water (to remove the iodine and bromine) and a few drops of hydrochloric acid, and evaporate to dryness; add a little water and (to remove the magnesia) some finely divided oxide of mercury, evaporate to dryness, and gently ignite until the oxide of mercury is just driven off; add a drop of hydrochloric acid, treat with a mixture of absolute alcohol and anhydrous ether, filter, concentrate the filtrate by evaporation, and set fire to the alcohol. If it burns with a carmine flame, LITHIA is present. By way of confirmation convert the lithia found into phosphate (§ 93, 3).

### 3. EXAMINATION FOR THOSE CONSTITUENTS WHICH ARE PRESENT IN MOST MINUTE QUANTITIES.

Evaporate 200 or 300 lbs. of the water in a large perfectly clean 260
iron vessel until the salts soluble in water begin to separate. If the mineral water contains no carbonate of soda, add sufficient of that substance to render the fluid distinctly alkaline. After evaporation filter the solution off, wash the precipitate, without adding the washings to the first filtrate, and

*a.* Examine the *precipitate* by the method given § 214 for sinter deposits;

*b.* Mix the *solution* with hydrochloric acid, to acid reaction,

heat, just precipitate the sulphuric acid which may be present with chloride of barium, filter, evaporate the filtrate to dryness, digest the residue with alcohol of 90 per cent., and examine the solution for CÆSIUM and RUBIDIUM according to § 93, at the end. Treat the residue insoluble in alcohol as follows. Make a hot concentrated solution of it in water, add ammonia in excess, filter if necessary, add iodide of potassium while still hot and allow to stand. If a precipitate forms test it for THALLIUM in the spectroscope.

## II. EXAMINATION OF THE SINTER-DEPOSIT.

### § 214.

1. Free the deposit from impurities, by picking, sifting, elu- 261
triation, &c., and from the soluble salts adhering to it, by washing with water; digest a large quantity (about 200 grammes) with water and hydrochloric acid (effervescence: CARBONIC ACID) at a very moderate heat until the soluble part is completely dissolved; dilute, let cool, filter, and wash the residue.

*a. Examination of the filtrate.*

*a.* Heat the larger portion to 70°, pass hydrosulphuric 262
acid for some time and also during the cooling. Allow to stand in a moderately warm place till the smell of the gas is almost gone and filter.

Wash and dry the precipitate, remove the greater part 263
of the free sulphur by digesting and washing with bisulphide of carbon, warm gently with yellow sulphide of potassium, dilute, filter, wash with water containing sulphide of potassium and precipitate the filtrate and washings with hydrochloric acid. Allow the precipitate to settle, filter it off, wash, dry, extract again with bisulphide of carbon, treat the residue (if any) together with the filter in a small porcelain dish with pure red fuming nitric acid, warm till the greater part of the acid is expelled, add excess of carbonate of soda, then a little nitrate of soda, fuse, treat the fusion with cold water, filter, wash with diluted alcohol, and test the aqueous solution for arsenic acid by **121** and **122**, the residue for ANTIMONY and TIN by dissolving in dilute hydrochloric acid and treating the solution with zinc free from lead in a platinum capsule (**123**).

If a residue remained on treating the hydrosulphuric 264
acid precipitate with sulphide of potassium, wash, remove from the filter by a jet of water, boil with a small quantity of dilute nitric acid, filter, wash and treat the contents of the filter first with hydrosulphuric acid—in order not to miss sulphate of lead which may possibly be present here—then test them for BARYTA and STRONTIA according to **255**. Mix the nitric acid solution with a little pure sulphuric acid, evaporate to dryness on a water-bath and treat with water; if a residue, it consists of sulphate of LEAD. To make sure, filter it off, wash, and see if it turns black with hydrosulphuric acid. Test the filtrate from the sulphate of lead with ammonia, and with ferrocyanide of potassium for COPPER.

Take a portion of the filtrate from the hydrosulphuric acid precipitate, evaporate it to dryness with excess of nitric acid on a water-bath, treat with nitric acid and water, filter and test the solution for PHOSPHORIC ACID with molybdate of ammonia. Transfer the remainder of the filtrate from the hydrosulphuric acid precipitate to a flask, add chloride of ammonium, then ammonia until the fluid is just alkaline, lastly sulphide of ammonium free from ammonia, fill the flask to the neck, close the mouth, allow to stand in a moderately warm place till the supernatant fluid is yellow without a shade of green, filter and wash with water containing sulphide of ammonium. Treat the precipitate with dilute hydrochloric acid and proceed to test for COBALT, NICKEL, IRON, MANGANESE, ZINC, ALUMINA, AND SILICA according to **152—160**. To examine for TITANIC ACID throw down a part of this hydrochloric solution with ammonia and treat the precipitate according to **222**. In the filtrate from the sulphide of ammonium precipitate throw down the LIME and STRONTIA and any BARYTA which may be present with carbonate and oxalate of ammonia, and test the precipitate for the two last by ENGELBACH'S method (end of § 99). Finally test the filtrate from the lime precipitate for MAGNESIA. **265**

*β.* Mix a portion considerably diluted, with chloride of barium, and allow it to stand 12 hours in a warm place. A white precipitate indicates SULPHURIC ACID.

*b. Examination of the residue.*

This consists of sand, hydrated silicic acid, clay, and organic matter; it may also contain sulphur (if the water contained hydrosulphuric acid), and sulphates of baryta and strontia. Boil with a solution of carbonate of soda and caustic soda to dissolve the HYDRATED SILICIC ACID and sulphur, filter, and treat on the paper with dilute hydrochloric acid to dissolve baryta and strontia and leave the clay and sand. Test the hydrochloric solution according to **256** for BARYTA and STRONTIA. **266**

2. To test for FLUORINE, the best way is to take a separate portion of the deposit. Mix with about half its weight of pure hydrate of lime (if carbonate of lime is not present in abundant quantity), ignite (blackening indicates organic matter), add water, and then acetic acid in excess, evaporate till the excess of acid is expelled, and proceed as directed **253**. **267**

3. Boil the deposit for a considerable time with concentrated potassa and filter. **268**

*a.* Acidify a portion of the filtrate with acetic acid, add ammonia, allow to stand 12 hours, and then filter off the precipitate of alumina and hydrated silicic acid, which usually forms; again add acetic acid in excess, and then solution of neutral acetate of copper. If a brownish precipitate is formed, this consists of APOCRENATE of copper. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color has changed to blue, and warm. If a bluish-green precipitate is produced, this consists of CRENATE of copper.

*b.* If you have detected arsenic, use the remainder of the alkaline fluid to ascertain whether the arsenic existed in the sinter as ARSENIOUS ACID or as ARSENIC ACID. (Compare § 134, 9).

## IV. Analysis of Soils.

### § 215.

Soils must necessarily contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant, the constituents of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition of that soil, and may accordingly save us, to some extent, the trouble of a qualitative analysis.

Viewed in this light, it would appear quite superfluous to make a qualitative analysis of soils still capable of producing plants; for it is well known that the ashes of plants contain almost invariably the same constituents, and the differences between them are caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is had also to the proportions of the constituents, and to the state in which they are present, an analysis of the kind, if combined with an examination of the physical properties of the soil, and a mechanical separation of its parts,* may give most useful results, enabling the analyst to judge sufficiently of the condition of the soil, to supersede the necessity of a quantitative analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances in a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which constituents are soluble in water;† which require an acid for their solution (in nature principally carbonic acid); and, finally, which are neither soluble in water, nor in acids, and are not, accordingly, in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting question to answer is whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether

* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition, compare F. SCHULZE, Journ. f. prakt. Chemie, 47, 241; also FRESENIUS's Quantitative Analysis, and E. WOLFF, Zeitschr. f. anal. Chem. 3, 85.

† It was formerly universally assumed that substances soluble in water, or in water containing carbonic acid, circulated freely in the soil so long as there existed agents for their solution; but since it has been discovered that arable soil possesses, like charcoal, the property of withdrawing from dilute solutions the bodies dissolved in them, this notion is exploded, and we now know that arable soil will retain with a certain force bodies otherwise soluble—from which we conclude that the aqueous extract of a soil cannot be expected to contain the whole of the substances present in that soil in a state immediately available for the plant. Neither can we expect to find these matters in the aqueous extract in the same proportion in which they are present in the soil, since the latter will readily give up to water those substances in regard to which its power of absorption has been satisfied, whilst it will more or less strongly retain others. But although, for this reason, the examination of the aqueous extract of a soil has no longer the same value as it was formerly considered to have, yet it is still useful to ascertain what substances a soil will actually give up to water. It is for this reason that I have retained the chapter on the preparation and examination of the aqueous extract.

resist the action of disintegrating agencies; and also what are the products which they yield upon their disintegration.*

In the analysis of soils, the constituents soluble in water, those soluble in acids, and the insoluble constituents, must be examined separately. The examination of the organic portion also demands a separate process.

The analysis is therefore properly divided into the following four parts:

1. *Preparation and Examination of the Aqueous Extract.*

§ 216.

About 1000 grammes of the air-dried soil are used for the pre- 269
paration of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty: in following the usual course, viz., digesting or boiling the earth with water, and filtering, the fine particles of clay are speedily found to impede the operation, by choking up the pores of the filter; they also almost invariably render the filtrate turbid, at least the portion which passes through first. I have found the following method proposed by F. SCHULZE (*loc. cit.*) the most practical. Close the neck of several middle-sized funnels with small filters of coarse blotting-paper, moisten the paper, press it close to the sides of the funnel, and then introduce the air-dried soil, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed; filling the funnels about two-thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back into the funnel. Let the operation proceed quietly. Fill the funnels again with water, and continue this process of lixiviation until the filtrates weigh twice or three times as much as the soil used. Collect the several filtrates in one vessel, and mix them intimately together. Keep a portion of the lixiviated soil.

Divide the aqueous solution into two parts, 1 (about two-thirds) and 2 (about one-third).

1. Evaporate in a porcelain dish to a small bulk and test as follows.

*a.* Filter off a portion, test the reaction of the filtrate, set 270
aside a part to test for organic matter (280), warm the rest and add nitric acid. Effervescence indicates an ALKALINE CARBONATE. Then test for CHLORINE with nitrate of silver.

*b.* Transfer the rest of the concentrated fluid from 1, together 271
with the precipitate which it usually contains, to a small dish (preferably of platinum), evaporate to dryness and heat the brownish residue cautiously till the organic matter is destroyed. In the presence of NITRATES a slight deflagration will be perceptible. Treat the residue as follows.

α. Test a small portion with carbonate of soda in the oxidizing flame for MANGANESE.

β. Warm the rest with water, add hydrochloric acid, (effervescence indicates carbonic acid), evaporate to dryness

* For more ample information on this subject the reader is referred to FRESENIUS's Chemie für Landwirthe, Forstmänner, und Cameralisten; Brunswick, Vieweg, 1847, p. 485.

to separate silicic acid, moisten with hydrochloric acid, add water, warm and filter.

*aa.* Wash the residue, which generally contains a little carbon, a little clay (if the aqueous extract was not clear), and also SILICIC ACID. To detect the latter, pierce the filter, wash the residue through, boil it with caustic soda, filter, saturate with hydrochloric acid, evaporate to dryness, and finally take up with water, when the silicic acid will remain behind.

*bb.* Test a part of the hydrochloric solution for SULPHURIC ACID with chloride of barium. Evaporate a second part with nitric acid and test for PHOSPHORIC ACID with molybdate of ammonia. Test a third part for IRON with sulphocyanide of potassium. To the rest add a few drops of sesquichloride of iron (to remove phosphoric acid), then ammonia till slightly alkaline, warm a little, filter, throw down the LIME with oxalate of ammonia and proceed to the examination for MAGNESIA, POTASSA, and SODA (§§ 196, 197). Finally examine a small quantity of the pure alkaline chlorides in the spectroscope for LITHIA.

Alumina is not likely to be found in the aqueous extract (F. SCHULZE never found it). But if you wish to test for it, boil the precipitate produced by ammonia with pure potassa in a platinum or silver dish, filter, acidify the filtrate with hydrochloric acid, add ammonia, and warm. 272

2. If you have found iron, acidify a portion with hydrochloric acid, and test half with ferricyanide of potassium, the other half with sulphocyanide of potassium, to see in what state the iron is present. Mix the rest of the aqueous extract with a little sulphuric acid, evaporate nearly to dryness on the water-bath, and test the residue for AMMONIA by means of hydrate of lime. If the aqueous extract is absolutely clear you may test it for ammonia directly by chloride of mercury, &c. (§ 92). 273

### 2. *Preparation and Examination of the Acid Extract.*

§ 217.

Heat about 50 grammes of the soil from which the part soluble in water has been removed as far as practicable* with moderately strong hydrochloric acid (effervescence indicates CARBONIC ACID) for several hours on the water-bath, filter, and make the following experiments with the filtrate, which is generally yellow from the presence of sesquichloride of iron. 274

1. Test a small portion with sulphocyanide of potassium for SESQUIOXIDE OF IRON, another with ferricyanide of potassium for PROTOXIDE OF IRON. 275

2. Test a small portion with chloride of barium for SULPHURIC ACID. Evaporate another portion to dryness, heat the residue to a temperature scarcely exceeding 100°, warm with nitric acid, filter off the silicic acid and test for PHOSPHORIC ACID with molybdate of ammonia in the cold.

* Complete lixiviation is generally impracticable.

3. Mix a large portion with ammonia to neutralize the free acid, then with yellowish sulphide of ammonium; let the mixture stand in a warm place, in a flask filled up to the neck, until the fluid looks yellow; then filter, and test the filtrate in the usual way for LIME, MAGNESIA, POTASSA, and SODA. 276

4. Dissolve the precipitate obtained in 3 in hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, add water, warm, filter, and examine the filtrate according to **150**, for IRON, MANGANESE, ALUMINA, and if necessary, also for lime and magnesia, which may have been thrown down by the sulphide of ammonium, in combination with phosphoric acid. 277

5. The separated SILICIC ACID obtained in 4 is usually colored by organic matter. It must, therefore, be ignited to obtain it pure.

6. If it is a matter of interest to ascertain whether the hydrochloric acid extract contains ARSENIC ACID, OXIDE OF COPPER, &c., treat the remainder of the solution with hydrosulphuric acid, as directed **262—264**. 278

7. Should you wish to look for FLUORINE, ignite a fresh portion of the earth, and proceed according to **230**.

### 3. *Examination of the Inorganic Constituents insoluble in Water and Acids.*

§ 218.

The operation of heating the lixiviated soil with hydrochloric acid (**274**) leaves still the greater portion of it undissolved. If you wish to subject this undissolved residue to a chemical examination, wash, dry, and sift, to separate the stones from the clay and sand; moreover, separate the two latter from each other by elutriation. Subject the several portions to the process given for silicates (§ 205). 279

### 4. *Examination of the Organic Constituents of the Soil.**

§ 219.

The organic constituents of the soil, which exercise so great an influence upon its fertility, both by their physical and chemical action, are partly portions of plants in which the structure may still be recognised (fragments of straw, roots, seeds of weeds, &c.), partly products of vegetable decomposition, which are usually called by the general name of HUMUS, but differ in their constituent elements and properties, according to whether they result from the decay of the nitrogenous or non-nitrogenous parts of plants—whether alkalies or alkaline earths have or have not had a share in their formation—whether they are in the incipient or in a more advanced stage of decomposition. To separate these several component parts of humus would be an exceedingly difficult task, which, moreover, would hardly repay the trouble; the

* Compare FRESENIUS'S Chemie für Landwirthe, Forstmänner, und Cameralisten; Brunswick, Vieweg, 1847, §§ 282—285.

following operations are amply sufficient to answer all the purposes of a qualitative analysis.

*a. Examination of the Organic Substances soluble in Water.*

Evaporate the reserved portion of 270 on the water-bath to 280
perfect dryness, and treat the residue with water. The ulmic, humic, and geic acids, which were present in the solution in combination with bases, remain undissolved, whilst CRENIC AND APOCRENIC ACIDS are dissolved in combination with ammonia; for the manner of detecting the latter acids, see 268.

*b. Treatment with Alkaline Carbonate.*

Dry a portion of the lixiviated soil, and sift to separate the 281
fragments of straw, roots, &c., and the small stones, from the finer parts; digest the latter for several hours at 80—90° with solution of carbonate of soda, and filter. Mix the filtrate with hydrochloric acid to acid reaction. If brown flakes separate, these proceed from ULMIC ACID, HUMIC ACID, or GEIC ACID. The larger the proportion of ulmic acid present the lighter will be the color of the flakes.

*c. Treatment with Caustic Alkali.*

Wash the soil boiled with solution of carbonate of soda (*b*) with 282
water, boil several hours with potassa, replacing the water as it evaporates, dilute, filter, and wash. Treat the brown fluid as in *b*. The ulmic and humic acids which separate now, are new products resulting from the action of boiling potassa upon ULMIN and HUMIN.

## V. DETECTION OF INORGANIC SUBSTANCES IN PRESENCE OF ORGANIC SUBSTANCES.

§ 220.

It will be readily conceived that the presence of organic substances may so far impede an analysis that it cannot be proceeded with until the organic matter has been totally destroyed; thus, for instance, the presence of organic coloring matter may completely conceal a change of color or a precipitate, again the presence of slimy matter may render filtration impossible. Difficulties of this kind are of constant occurrence in the examination of medicines, in the analysis of articles of food or of the contents of a stomach for inorganic poisons, and in the analysis of the inorganic constituents of vegetable or animal substances. In the following pages instructions will be given first for a general procedure, afterwards for several special cases.

1. *General Rules for the Detection of Inorganic Substances in Presence of Organic matters, which by their Color, Consistence or other Properties, impede the Application of the Reagents, or obscure the Reactions produced.*

§ 221.

We confine ourselves here, of course, to the description of the most generally applicable methods, leaving the modifications which

circumstances may require in special cases to the discretion of the analyst.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT THE SOLUTION IS DARK-COLORED OR OF SLIMY CONSISTENCE. 283

*a.* Heat a portion of the solution with hydrochloric acid on the water-bath, and gradually add chlorate of potassa until the mixture is decolorized and perfectly fluid; heat until it exhales no longer the odor of chlorine, then dilute with water, and filter. Examine the filtrate in the usual way, commencing at § 190. Compare also § 225. It is hardly necessary to observe that the state of oxidation of the metals founed cannot be determined; since suboxide of mercury, protoxide of tin, and protoxide of iron would be converted by the chlorate of potassa and hydrochloric acid into chloride of mercury, bichloride of tin, and sesquichloride of iron respectively.

*b.* Boil another portion of the solution for some time with nitric acid, filter and test the filtrate for SILVER and POTASSA. If the nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, &c., this method is often preferable to all others.

*c.* ALUMINA and SESQUIOXIDE OF CHROMIUM might escape detection by this method, because ammonia and sulphide of ammonium may fail to precipitate these oxides from fluids containing non-volatile organic substances. Should you have reason to suspect the presence of these oxides, mix a third portion of the substance with carbonate of soda and chlorate of potassa, and throw the mixture gradually into a red-hot crucible. Let the mass cool, then treat it with water, and examine the solution for chromic acid and alumina, the residue for alumina (§ 103).

*d.* Test a separate portion for AMMONIA with hydrate of lime.

*e.* Subject another portion to dialysis and examine the dialysate for acids.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE FLUID ADMITS OF FILTRATION. 284

Filter, and treat the filtrate either as directed § 189, or, should it require decoloration, according to **283**. The residue may be of various kinds.

*a.* It is FATTY. Remove the fatty matter by means of ether, and should a residue be left, treat this as directed § 175.

*b.* It is RESINOUS. Use alcohol instead of ether, or apply both liquids successively.

*c.* IT IS OF A DIFFERENT NATURE, *e.g.*, woody fibre, &c.

*α.* Dry, and ignite a portion in a porcelain or platinum vessel, avoiding too high a temperature, until total or partial incineration is effected; warm the residue with hydrochloric acid and a little nitric acid, dilute, and examine the solution as directed **109**; if a residue has been left, treat this according to § 203.

*β.* Examine another portion for the heavy metals and

acids, as directed 283—since with the method given in α. arsenic, cadmium, zinc, &c., may volatilize, besides mercury.

γ. Test the remainder for ammonia, by triturating with hydrate of lime.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART. 285

Treat the substance in the same manner as the residue in 284.

As regards the charred mass, 284 c, α, it is often advisable to boil the mass, carbonized at a gentle heat, with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ash.

4. The following method proposed by E. MILLON* is of very general application for the detection of metallic oxides when mixed with organic matter. Transfer the substance to a tubulated retort and add four times its weight of pure sulphuric acid. The retort should not be more than one-third full. Heat slowly till the mixture is homogeneous, and then placing a funnel tube in the tubulure of the retort and gently increasing the temperature, add nitric acid gradually. The object of this first operation is to decompose chlorides, which will take about half an hour. Now remove the mixture to a platinum dish and heat till the sulphuric acid, which by degrees loses its black color and turns orange or red, begins to escape. Add more nitric acid in small portions; after each addition the fluid will be decolorized, but it again turns darker on further heating. Continue adding nitric acid until no more coloration occurs, and finally expel the sulphuric acid, when you will obtain a saline mass to be analysed in the usual way. If the heat is moderated towards the end, according to MILLON none of the arsenic or mercury will be lost; but this cannot be depended on when much chlorides are present.

5. To separate salts from colloid organic matter, dialysis is very convenient.† The substance is sometimes first warmed with nitric acid or with chlorate of potassa and hydrochloric acid. (Compare § 224.)

### 2. *Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, &c., in Chemico-legal Cases.*‡

### § 222.

The chemist is sometimes called upon to examine an article of food, the contents of a stomach, a dead body, &c., with a view to detect the presence of some poison, and thus to establish the fact of poisoning; but it is more frequently the case that the question put to him is of a less general nature, and that he is called upon to determine whether a certain substance placed before him contains a metallic poison; or, more pointedly still, whether it contains arsenic or hydrocyanic acid, or some other particular poison—as 286

* Journ. de Pharm. et de Chim. 46, 33. Zeitschr. f. anal. Chem. 4, 208.

† Compare O. REVEIL, Zeitschr. f. anal. Chem. 4, 266; BIZIO, *Ibid.* 5, 51; RIEDERER, *Ibid.* 7, 517.

‡ Compare FRESENIUS, Ann. d. Chem. u. Pharm. 49, 275; and FRESENIUS and v. BABO, Ann. d. Chem. u. Pharm. 49, 287.

it may be that the symptoms point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question.

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether a certain poison, *e.g.* arsenic, is present or not, if he adopts a course of proceeding which will not only permit the detection of the one poison specially named, the presence of which may perhaps be suspected on insufficient grounds, but will moreover inform him as to the presence or absence of other similar poisons.

But we must not go too far in this direction either; if we were to attempt to devise a method that should embrace all poisons, we might unquestionably succeed in elaborating such a method at the writing-desk; but practical experience would but too speedily convince us that the intricate complexity inseparable from such a course, must necessarily impede the easy execution of the process, and impair the certainty of the results, to such an extent indeed, that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances permit usually at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, I give here,—

1. A method which ensures the detection of the minutest traces of arsenic, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for alkaloids.

3. A method to effect the detection of phosphorus, which does not interfere with the examination for other poisons.

This part of the work does not, therefore, profess to supply a complete guide in every possible case of chemico-legal investigations. But the instructions given in it are the tried and proved results of my own practice. Moreover, they will generally be found sufficient, the more so as in the Section on the alkaloids, I give the description of the best processes by which the detection of these latter poisons in criminal cases may be effected.

Where you have no indications at all of the sort of poison to be looked for, begin by carefully inspecting the substance with the aid of a microscope if necessary, by noting the odor, reaction, &c., and then if the circumstances do not point to examining different portions for the different classes of poisons, proceed to test for hydrocyanic acid and phosphorus (a distillation usually suffices for the detection of both), afterwards for alkaloids, and finally for metallic poisons. As an obvious matter of caution, you should always reserve one-third of the substance, after weighing and mixing, for contingencies.

## I. Method for the Detection of Arsenic (with due Regard to the possible Presence of other Metallic Poisons).

### § 223.

Of all metallic poisons arsenic is the most dangerous, and at 287
the same time the one most frequently used, more particularly for the wilful poisoning of others. And again, among the compounds of arsenic, arsenious acid occupies the first place, because it kills even in small doses, it does not betray itself, or at least very slightly, by the taste, and it is but too readily procurable.

As arsenious acid dissolves in water only sparingly, and—on account of the difficulty with which moisture adheres to it—very slowly, the greater portion of the quantity swallowed exists usually in the body still in the undissolved state; as, moreover, the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—no matter what opinion may be entertained about the normal presence of arsenic in the bones, &c.—this much is certain, that *arsenious acid in grains or powder* is never normally present in the body, the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious acid in substance—and this end may indeed usually be attained.

*A. Method for the Detection of undissolved Arsenious Acid.*

1. If you have to examine food, vomit, or some other matter of 288
the kind, after weighing it mix the whole as uniformly as may be practicable, reserve one-third for contingencies, and mix the other two-thirds in a porcelain dish with distilled water, with a stirring rod; let the mixture stand a little, then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat this latter operation several times, if possible with the same fluid, pouring it from the second dish back into the first and so on. Finally, wash once more with pure water, best in a glass dish, remove the fluid as far as practicable, and try whether you can find in the dish small, white, hard grains which feel gritty under the glass rod. If not proceed as directed § 224 or § 225. But if so, pick out the grains, or some of them, with a pair of pincers, or wash them if they are very minute in a watch-glass, dry, weigh them, and heat a small portion in a glass tube, another small portion with a splinter of charcoal (compare § 132, 2 and 11). If you obtain in the former experiment a white sparkling sublimate consisting of octahedrons and tetrahedrons, in the latter experiment an arsenical mirror, you are quite safe in concluding that the grains consist of arsenious acid. If you wish to determine the quantity of the arsenic, or to test for other metallic poisons, unite the contents of both dishes, and proceed as directed § 224 or § 225.

2. If a stomach is submitted to you for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and (*a*), search the inside coat for small, white, hard, sandy grains. The spots occupied by such grains are often reddened; the grains are also frequently found firmly imbedded in the membrane. (*b*) Mix the contents in the dish uniformly, weigh them, put aside one-third

for contingencies, and treat the other two-thirds as in 1. The same course is pursued also with the intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious acid cannot be found in grains, if the poison has been introduced through the mouth. If you have found grains of the kind described, examine them as directed in 1; if not, or if you wish to test also for other metallic poisons, proceed according to § 224 or § 225.

*B. Method of detecting soluble Arsenical and other Metallic Compounds by means of Dialysis.*

§ 224.

If method *A* has failed to show the presence of arsenious acid 289
in the solid state, and the process described in § 225, in which the organic substances are totally destroyed by chlorate of potassa and hydrochloric acid, is at once resorted to, the operator must, of course, in the event of the presence of arsenic being revealed, give up all notion of ascertaining, as far as the portion operated upon is concerned, in what form the poison has been administered; as the process will give a solution containing arsenic acid, no matter whether the poison was originally present in that form, or as arsenious acid, or as sulphide, or in the metallic state, &c. This defect may be remedied, however, by interpolating a dialytic experiment between *A* and *C*.

The experiment requires the apparatus shown in § 8, fig 5. The hoop is made of wood or, better, of gutta percha; it is 2 inches in depth, and 8 or 10 inches in diameter. The residue and fluid of § 223, *A*, having been mixed according to the circumstances with two-thirds of the stomach, intestinal canal, &c., cut small, and digested for twenty-four hours at about 32°, is poured into the dialyser to a depth of not more than half an inch. The dialyser is then floated in a basin containing about 4 times as much water as the fluid to be dialysed amounts to. After 24 hours one-half or three-fourths of the crystalloids will be found in the external water, which generally appears colorless. Concentrate this by evaporation on the water-bath, acidify the greater part with hydrochloric acid, treat with sulphuretted hydrogen, and proceed generally as directed 291 *et seq.* If an arsenical compound soluble in water (or some other soluble metallic salt) is present, the corresponding sulphide is obtained almost pure. By floating the dialyser successively on fresh supplies of water, the whole of the soluble crystalloids present may finally be withdrawn. If arsenic is found, test the remainder of the concentrated dialysate according to § 134, 9, to see whether arsenious or arsenic acid is present.

It is generally best to examine the exhausted contents of the dialyser at once according to § 225 for metals, but in some cases, as for instance when you wish to determine the state of oxidation or combination of compounds of arsenic or other metals, it is preferable to heat the matter first with dilute hydrochloric acid and to dialyse it again.

Instead of interpolating the dialysis at this stage, you may wait till the close of *C*, and then if a metallic poison has been found and

you wish to ascertain its state of combination, you may recur to this paragraph, using the reserved one-third for the experiment.

*C. Method for the Detection of Arsenic in whatever Form it may exist, which allows also of its Quantitative Determination, and of the Detection of all other Metallic Poisons.**

§ 225.

If you have found no arsenious acid in substance by the method described in *A*, nor a soluble arsenic compound by dialysis, evaporate the mass in the porcelain dish, on the water-bath, to a pasty consistence; adding, if occasion requires, two-thirds of the stomach and intestines cut small, provided this has not been done already in the process of dialysis.

In examining other parts of the body (the lungs, liver, &c.), cut them also into small pieces, and use two-thirds for the analysis.

The process is divided into nine parts.†

1. *Decoloration and Solution.*

Add to the matters in the porcelain dish, which may amount 290
to, say 100 or 250 grammes, an amount of hydrochloric acid of 1·12 sp. gr., about equal to or somewhat exceeding the weight of the dry substances present, and sufficient water to give to the entire mass the consistence of a thin paste. The quantity of hydrochloric acid added should never exceed one-third of the entire liquid present. Heat the dish now on the water-bath, adding every five minutes about two grammes of chlorate of potassa to the hot fluid, with stirring, until the contents of the dish are light yellow, and also perfectly homogeneous and fluid; replace the evaporating water from time to time. When this point is attained, add again a portion of chlorate of potassa, and then remove the dish from the water-bath. When the contents are quite cold, transfer them cautiously to a linen strainer or a white filter, according to the quantity; allow the whole of the fluid to pass through, and heat the filtrate on the water-bath with renewal of the evaporating water, until the smell of chlorine has gone off or nearly so. Wash the residue well with hot water, and dry it; then mark it I., and reserve for further examination, according to 303. Evaporate the washings on the water-bath to about 100 grammes, add this, together with any precipitate that may have formed therein, to the principal filtrate.

2. *Treatment of the Solution with Hydrosulphuric Acid* (Separation 291
of the Arsenic as Tersulphide, and of all the Metals of Groups V. and VI. in forms of Sulphides).

Transfer the fluid obtained in 1, which amounts to three or four times the quantity of the hydrochloric acid used, to a flask, heat this on the water-bath to 70°, and transmit through it, for

* This method is essentially the same as that which was published in 1844 by L. v. BABO and myself; compare Ann. d. Chem. u. Pharm., 49, 308. I have since that time had frequent occasion to apply it; I have also had it tried by others, under my own inspection, and *I have invariably found it to answer the purpose perfectly.*

† I need hardly observe, that in an analysis of this kind, too much care cannot be taken to insure the purity of the reagents and the cleanliness of the apparatus.

about 12 hours, a slow stream of washed hydrosulphuric acid, then let the mixture cool, continuing the transmission of the gas; rinse the delivery pipe with some ammonia, add the ammoniated solution thus obtained, after acidifying, to the principal fluid, cover the flask lightly with unsized paper, and put it in a moderately warm place (about 30°) until the odor of hydrosulphuric acid has nearly disappeared. Collect the precipitate obtained in this manner on a filter, and wash with water containing hydrosulphuric acid until the washings are quite free from chlorine. Concentrate the filtrate and washings. If a precipitate forms, filter it off, wash and add it to the principal hydrosulphuric acid precipitate. Mix the concentrated fluid in a proper sized flask with ammonia to alkaline reaction, then with sulphide of ammonium, closely cork the flask, which must now be nearly full, and reserve it for further examination according to **307**.

3. *Purification of the Precipitate produced by Hydrosulphuric Acid.* **292**

The precipitate obtained in 2 contains the whole of the arsenic and all the other metals of the fifth and sixth groups, in the form of sulphides, and also organic matter and free sulphur. Dry it with the filter completely in a small dish, over the water-bath, add pure fuming nitric acid (free from chlorine), drop by drop, until the mass is completely moistened, then evaporate on the water-bath to dryness. Moisten the residue uniformly all over with pure concentrated sulphuric acid, previously warmed; then heat for two or three hours on the water-bath, and finally with an air- sand- or oil-bath at a somewhat higher, though still moderate temperature (170°), until the charred mass becomes friable, and a small sample of it—to be returned afterwards to the mass—when mixed with water and then allowed to subside, gives a colorless fluid; should the aqueous fluid be brownish, or should the residue consist of a brown oily liquid, add to the mass some cuttings of pure Swedish filtering-paper, and continue the application of heat. You may raise the heat till fumes of sulphuric acid begin to escape without fear of loss of arsenic. By attending to these rules you will always completely attain the object in view, viz., the destruction of the organic substances, without loss of any of the metals. Warm the residue on the water-bath with a mixture of 8 parts of water and 1 part of hydrochloric acid, filter, wash the undissolved part thoroughly with hot water, containing a little hydrochloric acid, and add the washings, concentrated if necessary, to the filtrate.

Dry the washed carbonaceous residue, then mark it II., and reserve it for further examination according to **304**.

4. *Preliminary Examination for Arsenic and other Metallic Poisons of Groups V. and VI.* (Second Precipitation with Hydrosulphuric Acid.) **293**

The clear and colorless or, at the most, somewhat yellowish fluid obtained in 3 contains all the arsenic in form of arsenious acid, and may contain also tin, antimony, mercury, copper, bismuth, and cadmium. Supersaturate a small portion gradually with a

mixture of carbonate of ammonia and ammonia, and observe whether a precipitate is produced, acidify with hydrochloric acid, which will redissolve the precipitate that may have been produced by ammonia; then return the sample to the principal fluid, and treat the latter with hydrosulphuric acid, first at a gentle heat, afterwards without heat, according to **291**.

This process may lead to three different results, which are to be carefully distinguished.

*a. The hydrosulphuric acid fails to produce a precipitate;* but on standing a trifling white or yellowish-white precipitate separates. In this case probably no metals of Groups V. and VI. are present. Nevertheless, treat the filtered and washed precipitate as directed **297**, to guard against overlooking even the minutest traces of arsenic, &c. **294**

*b. A precipitate is formed, of a pure yellow color;* like that of tersulphide of arsenic. Take a small portion of the fluid, together with the precipitate suspended therein, add some ammonia, and shake for some time without heating. If the precipitate dissolves readily and, with the exception of a trace of sulphur, completely, and if in the preliminary examination, (**293**) carbonate of ammonia has failed to produce a precipitate, arsenic alone is present, and no other metal (at least, if any tin or antimony is present, it is not worth mentioning). Mix the solution of the small sample in ammonia, with hydrochloric acid to acid reaction, return this to the fluid containing the principal precipitate and proceed as directed **297**. If, on the other hand, the addition of ammonia to the sample completely or partially fails to redissolve the precipitate, or if, in the preliminary examination (**293**), carbonate of ammonia has produced a precipitate, there is reason to suppose that another metal is present, perhaps with arsenic. In this latter case also, add to the sample in the test-tube hydrochloric acid to acid reaction, return it to the fluid containing the principal precipitate, and proceed as directed **298**. **295**

*c. A precipitate is formed of another color.* In that case you have to assume that other metals are present, perhaps with arsenic. Proceed as directed **298**. **296**

5. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, when the Results of* **295** *lead to the Assumption that Arsenic alone is present.* (Determination of the Weight of the Arsenic.) **297**

As soon as the fluid precipitated according to **293** has nearly lost the smell of sulphuretted hydrogen, collect the yellow precipitate on a small filter, wash thoroughly, pour upon the still moist precipitate solution of ammonia, and wash the filter—on which, in this case, nothing must remain undissolved, except some sulphur—thoroughly with dilute ammonia; evaporate the fluid in a small accurately tared porcelain dish, on the water-bath and dry the residue at 100° until the weight is constant. The final weight represents the quantity of sulphide of arsenic if upon the subsequent reduction this is found to be pure; in that case, multiply the weight by ·8049 to obtain the corresponding amount of arse-

nious acid, or by ·6098 to obtain the corresponding amount of metallic arsenic. Treat the residue in the dish according to **300**.

6. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, when the Results of* **295** *or* **296** *lead to the Assumption that another Metal is present—perhaps with Arsenic.* (Separation of the Metals from each other. Determination of the Weight of the Arsenic.) **298**

If you have reason to suppose that the fluid precipitated according to **293** contains other metals, perhaps with arsenic, proceed as follows:—As soon as the precipitation is thoroughly accomplished, and the smell of sulphuretted hydrogen has nearly gone off, collect the precipitate on a small filter, wash thoroughly, pierce the filter, and wash all the precipitate into a small flask, using the least possible quantity of water; add to the fluid in which the precipitate is now suspended, first ammonia, then some yellowish sulphide of ammonium, and let the mixture digest for some time at a gentle heat. Should part of the precipitate remain undissolved, filter this off, wash, pierce the filter, rinse off the residuary precipitate, mark it III., and reserve for further examination according to **305**. Evaporate the filtrate, together with the washings, in a small porcelain dish to dryness. Treat the residue with some pure fuming nitric acid (free from chlorine), nearly drive off the acid by evaporation, then add, as C. MEYER was the first to recommend, a solution of pure carbonate of soda, in small portions till in excess. Add now a mixture of 1 part of carbonate and 2 parts of nitrate of soda in sufficient, yet not excessive quantity, evaporate to dryness, and heat the residue very gradually to fusion. Let the fused mass cool, and take it up with cold water. If a residue re- **299** mains undissolved, filter, wash with a mixture of equal parts of spirit of wine and water, mark it IV., and reserve for further examination, according to **306**. Mix the solution which contains all the arsenic as arsenate of soda, with the washings, previously freed from alcohol by evaporation, add cautiously pure dilute sulphuric acid to strongly acid reaction, evaporate in a small porcelain dish, and, when the fluid is strongly concentrated, add again sulphuric acid, to see whether the quantity first added has been sufficient to expel all nitric acid and nitrous acid; heat now cautiously until heavy fumes of hydrated sulphuric acid begin to escape; then let the liquid cool, add water, transfer the solution to a small flask, keep heated at 70°, and conduct into it for at least 6 hours, a slow stream of washed hydrosulphuric acid. Let the mixture finally cool, continuing the transmission of the gas all the while. If arsenic is present, a yellow precipitate will form. When the precipitate has completely subsided, and the fluid has nearly lost the smell of sulphuretted hydrogen, filter, wash the precipitate, dry it, extract the free sulphur with pure bisulphide of carbon, dissolve in ammonia, and treat the solution according to **297**, in order to determine the weight of the arsenic.

### 7. *Reduction of the Sulphide of Arsenic.*

The production of metallic arsenic from the sulphide, which **300** may be regarded as the keystone of the whole process, demands

the greatest care and attention. The method recommended § 132, 12, viz., to fuse the arsenical compound, mixed with cyanide of potassium and carbonate of soda, in a slow stream of carbonic acid gas, is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with any other body, more particularly antimony; on which account it is more especially adapted for medico-legal investigations.

Take care to have the whole apparatus filled with carbonic acid, and to give the proper degree of force to the gaseous stream, before applying heat. Instead of the gas generating apparatus shown § 132, 12, you may use the simpler one figured in the margin; the clip being provided with an adjusting screw, and the stoppers being of caoutchouc. A gas generating apparatus which does not allow of the current being regulated is not adapted for the present purpose.

Fig. 44.

Do not reduce the whole of the sulphide of arsenic at once, so that if you wish afterwards you may repeat the reduction several times. If there is too little sulphide of arsenic to be divided, dissolve it in a few drops of ammonia, add a small quantity of carbonate of soda, evaporate to dryness on the water-bath with stirring and take a portion of the mass for the reduction.

Otto recommends* to convert the sulphide into arsenic acid, 301
before proceeding to the reduction. The following is the process given by him to effect the conversion: Pour concentrated nitric acid over the sulphide in the dish, evaporate, and repeat the same operation several times if necessary, then remove every trace of nitric acid by repeatedly moistening the residue with water, and drying again, treat the residue with a few drops of water, add carbonate of soda in powder, to form an alkaline mass, and thoroughly dry this in the dish, with frequent stirring, taking care to collect the mass within the least possible space in the middle of the dish. The dry mass thus obtained is admirably adapted for reduction. I can fully confirm this statement; but I must once more repeat that it is indispensable for the success of the operation that the residue should be perfectly free from *every trace* of nitric acid or nitrate, since otherwise deflagration is sure to take place during the fusion with cyanide of potassium, and, of course, the experiment will fail.

* Anleitung zur Ausmittelung der Gifte, von Dr. Fr. Jul. Otto.

When the operation is finished, cut off the reduction tube at *c* 302
(fig. 45), set aside the fore part, which contains the arsenical mirror, put the other part of the tube into a cylinder, pour water over it, and let it stand some time; then filter the solution obtained, add to the filtrate hydrochloric acid to acid reaction; then conduct some hydrosulphuric acid into it, and observe whether this produces a

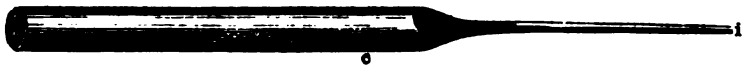


Fig. 45.

precipitate. In cases where the reduction of the sulphide of arsenic has been effected directly, without previous conversion to arsenic acid, a trifling yellow precipitate will usually form; had traces of antimony been present, the precipitate would be orange-colored and insoluble in carbonate of ammonia. After all the soluble salts of the fused mass have been dissolved out, examine the metallic residue which may be left, for traces of tin and antimony (nothing but traces of these two metals could be present here if the instructions given have been strictly followed). Should appreciable traces of these metals, or either of them, be found, proper allowance must be made for this in calculating the weight of the arsenic.

8. *Examination of the reserved Residues, for other Metals of the Fifth and Sixth Groups.*

*Residue I.* This may contain chloride of silver and sulphate of 303
lead, possibly also binoxide of tin and sulphate of barium. Incinerate it in a porcelain dish, burn the carbon with the aid of nitrate of ammonia, extract the residue with water, dry the part left undissolved, then fuse it with carbonate of soda and cyanide of potassium in a porcelain crucible. When cold exhaust with water, treat the residue with dilute acetic acid to extract any carbonate of baryta, warm any residue which may still be left with nitric acid, and proceed according to § 181. Test the acetic acid solution for baryta with solution of sulphate of lime.

*Residue II.* This may contain lead, mercury, and tin, possibly 304
also, antimony and bismuth. Heat it for some time with nitrohydrochloric acid, and filter the solution; wash the residue with water, at first mixed with some hydrochloric acid, add the washings to the filtrate, and treat the mixture with hydrosulphuric acid. Should a precipitate form, examine it according to § 191. Incinerate the residue insoluble in nitrohydrochloric acid, fuse the ash with cyanide of potassium and treat the fused mass as directed **303**.

*Residue III.* Examine for the metals of the fifth group according 305
to § 193.

*Residue IV.* This may contain tin and antimony, perhaps also 306
copper. Treat it as directed **123**. If the color of the residue was black (oxide of copper), treat the reduced metals according to § 181.

9. *Examination of the reserved filtrate for Metals of the Third and Fourth Groups, especially for Zinc, Chromium, and Thallium.**

*a.* The filtrate from the hydrosulphuric acid precipitate, has already been mixed with sulphide of ammonium. The addition of this reagent is usually attended with the formation of a precipitate consisting of sulphide of iron and phosphate of lime, but which may possibly also contain sulphide of zinc, sulphide of thallium and hydrated oxide of chromium. Filter it off, wash with water containing sulphide of ammonium, dissolve by warming with hydrochloric acid and a little nitric acid, evaporate the filtrate with sulphuric acid in a retort till quite thick, and test the distillate with iodide of potassium and bichloride of platinum, and also in the spectroscope, for THALLIUM (§ 113, *b*), as a portion of this metal may have escaped with the hydrochloric acid. Treat the residue in the retort with water, filter, add carbonate of soda to alkaline reaction, and then excess of solution of cyanide of potassium (free from sulphide). Heat for some time, filter, reserve the residue on the filter (*a*), mix the filtrate with sulphide of ammonium, and examine the precipitate for THALLIUM in the spectroscope. Evaporate the filtrate together with the residue *a* under a good draught with excess of sulphuric acid, till some of the latter begins to escape, dilute, filter, throw down with ammonia and sulphide of ammonium, and test the precipitate for ZINC and SESQUIOXIDE OF CHROMIUM according to **156—159**. 307

*b.* The fluid filtered from the precipitate produced by sulphide of ammonium (**307**) may contain all the chromium, as sulphide of ammonium fails to precipitate sesquioxide of chromium completely from solutions containing organic matter. To detect it, evaporate to dryness, ignite, mix the fixed residue with 3 parts of chlorate of potassa and 1 part of carbonate of soda, and project the mixture into a crucible heated to moderate redness. Allow the mass to cool, and boil with water, when a yellow coloration of the fluid will indicate chromium. For confirmatory tests see § 138. 308

## II. METHOD FOR THE DETECTION OF HYDROCYANIC ACID.

### § 226.

Under the term hydrocyanic acid we include cyanide of potassium, which acts in the same way, and being extensively used in the arts is much more readily procurable. As hydrocyanic acid may easily decompose in presence of the matter of food or the contents of the stomach, the analyst must proceed without unnecessary delay. However, the acid does not decompose with such extreme rapidity as might be imagined, and in fact it is some time before the whole of it is lost.† 309

* With reference to the poisonous action of thallium, compare LAMY, Journ. f. prakt. Chem. 91, 366. And for the electrolytic method of discovering thallium in chemico-legal cases, see MARMÉ, Zeitschr. f. anal. Chem. 6, 503.

† Thus I succeeded in separating a notable quantity of hydrocyanic acid from the stomach of a man who had poisoned himself with that acid in very hot weather, and whose intestines were not handed to me till 36 hours after death. Again, a dog was

Although hydrocyanic acid betrays its presence, even in minute quantities, by its odor, still this sign must never be looked upon as conclusive. On the contrary, to adduce positive proof of the presence of the acid, it is always indispensable to separate it, and to convert it into certain known compounds.

The method of accomplishing this, which I am about to describe, is based upon distillation of the acidified mass, and examination of the distillate for hydrocyanic acid. Now, as the non-poisonous salts, ferro- and ferricyanide of potassium, give by distillation likewise a product containing hydrocyanic acid, it is indispensable—as OTTO observes—first to ascertain whether one of these salts may not be present. To this end, stir a small portion of the mass to be examined with water, filter, acidify the filtrate with hydrochloric acid, and test a portion of it with sesquichloride of iron, another with sulphate of protoxide of iron. If no blue precipitate or coloration forms in either, soluble ferro- and ferricyanides are not present, and you may safely proceed as follows. If a reaction is obtained proceed according to **314**.

Test, in the first place, the reaction of the mass under examination; if necessary, after mixing and stirring it with water. If it is not already strongly acid, add solution of tartaric acid until the fluid strongly reddens litmus-paper; introduce the mixture into a retort, and place the body of the retort, with the neck pointing upwards, in an iron or copper vessel, the bottom of which is covered with a cloth; fill the vessel with a solution of chloride of calcium, and apply heat, so as to cause gentle ebullition of the contents of the retort. Conduct the vapors passing over, with the aid of a tight-fitting tube, bent at a very obtuse angle, through a LIEBIG'S condenser,* and receive the distillate in a small weighed flask. When about 15 c.c. of distillate has passed over, remove the receiver, and replace it by a somewhat larger flask, also previously tared. Weigh the contents of the first receiver now, and proceed as follows: **310**

*a.* Mix one-fourth with potassa to strongly alkaline reaction, add a small quantity of solution of sulphate of protoxide of iron, mixed with a little sesquichloride of iron, digest a few minutes at a very gentle heat, and supersaturate finally with hydrochloric acid. A blue precipitate indicates hydrocyanic acid. If only a very small quantity is present the fluid is at first merely colored greenish, but on standing it will deposit blue flakes. **311**

*b.* Treat another fourth as directed § 155, 7, to convert the hydrocyanic acid into sulphocyanide of iron. As the distillate might, however, contain acetic acid, do not neglect to add at the end of the process a little more hydrochloric acid, in order to destroy the influence of the acetate of ammonia. **312**

*c.* If the experiments *a* and *b* have demonstrated the presence of hydrocyanic acid, and you wish now also to approxi- **313**

poisoned with hydrocyanic acid, and the contents of the stomach, mixed with the blood, were left for 24 hours exposed to an intense summer heat, and then examined: the acid was still detected.

* In testing for phosphorus at the same time, the condenser must be entirely of glass, and the operation must be conducted in a perfectly dark room. Compare 318.

mately determine its quantity, continue the distillation as long as the fluid passing over contains hydrocyanic acid; add one-half of the contents of the second receiver to the remaining half of the contents of the first, mix the fluid with nitrate of silver, then with ammonia in excess, and finally with nitric acid to strongly acid reaction. Allow the precipitate which forms to subside, collect on a tared filter dried at 100°, wash the precipitate, dry it thoroughly at 100°, and weigh. Ignite the weighed precipitate in a small porcelain crucible, to destroy the cyanide of silver, fuse the residue with carbonate of soda and potassa (to effect the decomposition of the chloride of silver which it may contain), boil the mass with water, filter, acidify the filtrate with nitric acid, and precipitate with nitrate of silver; determine the weight of the chloride of silver which may precipitate, and deduct the amount found from the total weight of the chloride and cyanide of silver. The difference gives the quantity of the latter; by multiplying this by ·2017, you find the corresponding amount of anhydrous hydrocyanic acid; and by multiplying this again by 2—as only one-half of the distillate has been used—you find the total quantity of hydrocyanic acid which was present in the examined mass. Instead of decomposing the fused silver precipitate by fusion with carbonate of soda and potassa, it may be reduced also by means of zinc, with addition of dilute sulphuric acid, and the chlorine determined in the filtrate.

Instead of pursuing this indirect method, you may also determine the quantity of the hydrocyanic acid by the following direct method: introduce half of the distillate into a retort, together with powdered borax; distil to a small residue, and determine the hydrocyanic acid in the distillate as cyanide of silver. Hydrochloric acid can no longer be present in this distillate, as the borax retains it in the retort (WACKENRODER).

When ferro- or ferricyanides have been detected, J. OTTO 314
recommends to slightly acidify the mass, to add precipitated carbonate of lime in excess and to distil it at 40° or 50° on a water-bath. The hydroferro- and hydroferricyanic acids are retained by the lime of the carbonate of lime, the hydrocyanic acid distils over. The distillation cannot be effected directly over the flame, as hydrocyanic acid would pass into the distillate even when ferrocyanides or ferricyanides alone were present.

### III. METHOD FOR THE DETECTION OF PHOSPHORUS.

### § 227.

Since phosphorus paste has been employed to poison mice, &c., 315
and the poisonous action of lucifer matches has become more extensively known, phosphorus has not unfrequently been resorted to as an agent for committing murder. The chemist is therefore occasionally called upon to examine some article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state*, or to the production of such re-

actions as will enable him to infer the presence of *free phosphorus*; since the mere finding of phosphorus in form of phosphates would prove nothing, as phosphates invariably form constituents of animal and vegetable bodies.

### A. *Detection of Unoxidized Phosphorus.*

1. Ascertain in the first place whether the presence of phos- 316
phorus is indicated by its smell, or by its luminosity in the dark. To this end take care to increase the contact of the phosphorus with the air, by rubbing, stirring, or shaking.

2. Put a little of the substance into a flask, fasten to the loosely 317
inserted cork a strip of filtering-paper moistened with neutral solution of nitrate of silver, and heat to 30° or 40°. If the paper does not turn black, even after some time, no unoxidized phosphorus is present, and there is consequently no need to try 3 and 4, but the operator may at once pass on to **324**. If, on the other hand, the paper turns black, this is no positive proof of the presence of phosphorus, as hydrosulphuric acid, formic acid, putrifying matters, &c., will also cause blackening of the paper. Treat therefore the principal mass of the substance now by the methods 3 and 4. (To ascertain whether the blackening proceeds from the presence of hydrosulphuric acid, try the reaction with a strip of paper moistened with solution of lead or with terchloride of antimony.)—T. SCHERER.*

3. As the luminosity of phosphorus is always one of the most 318
striking proofs of the presence of that element in the unoxidized state, examine a large portion of the substance by the following excellent and approved method, recommended by E. MITSCHERLICH.†

Mix the substance with water and some sulphuric acid or—if you are testing for hydrocyanic acid at the same time—tartaric acid, and subject the mixture to distillation in a flask, *A* (fig. 46). This flask is connected with an evolution tube, *b*, and the latter again with a glass condensing tube, *c c c*, which passes through the bottom of a cylinder, *B*, in which it is fastened by means of a cork, and opens into a glass vessel, *C*. Cold water is made to run from *D* through a stopcock, into a funnel, *i*, the lower end of which rests upon the bottom of *B*; the water flows off through *g*.‡

Now, if the substance in *A* contains phosphorus, there will appear, in the dark, at the point *r*, a strong luminosity, usually a luminous ring. If you take for distillation 150 grm. of a mixture containing only 1·5 mgrm. of phosphorus, and accordingly only 1 part in 100,000, you may distil over 90 grm., which will take at least half an hour—without the luminosity ceasing. MITSCHERLICH, in one of his experiments, stopped the distillation after half an hour, allowed the flask to stand uncorked a fortnight, and then recommenced the distillation: the luminosity was as strong as at first.

If the fluid contains substances which prevent the luminosity of phosphorus, such as ether, alcohol, or oil of turpentine, no luminosity is observed so long as these substances continue to distil over.

* Ann. d. Chem. u. Pharm. 112, 214. † Journ. f. prakt. Chem. 66, 238.

‡ A glass LIEBIG'S condenser may of course be used instead of this apparatus.

In the case of ether and alcohol, however, this is soon effected, and the luminosity accordingly very speedily makes its appearance; but oil of turpentine positively stops the reaction.

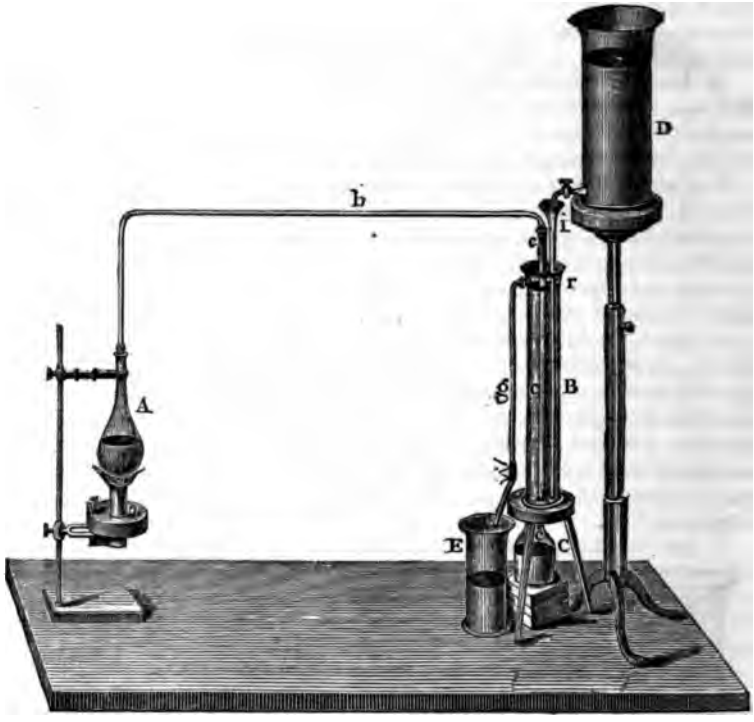


Fig. 46.

After the termination of the process, globules of phosphorus are 319
found at the bottom of the receiver. MITSCHERLICH obtained from 150 grm. of a mixture containing ·02 grm. phosphorus, so many globules of that body, that the tenth part of them would have been amply sufficient to demonstrate its presence. In medico-legal investigations these globules should first be washed with alcohol, then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that they really consist of phosphorus; the remainder, together with a portion of the fluid which shows the luminosity upon distillation, should be sent in with the report.

The operation should be conducted in a dark place, best in the evening. Where it is performed in the daytime, care should be taken to close all avenues to the entrance of light, as where this is not effectively done, the rays of light entering through some chink or crevice, may chance to be reflected by the glass vessel or by the fluids, and thus lead to deception. It is advisable to pass the evolution tube at *b*, through the aperture of a screen, to guard effectively against reflection of light from the lamp. These precautionary

measures are of course necessary only where very minute traces of phosphorus are to be detected.

The residue left in the flask is then examined for phosphorous acid as directed **324**. The distillate also may be further examined in the same way, to confirm the presence of phosphorus, or to show the presence of phosphorous acid formed by the oxidation of phosphorus fumes.*

4. Put another portion of the substance, with addition of water **320** if necessary, into a flask with doubly perforated cork, add dilute sulphuric acid to acid reaction, conduct washed carbonic acid gas (evolved most conveniently from the evolution flask shown p. 159 or p. 314) in a slow stream, into the flask, through a glass tube reaching nearly to the bottom, and let the gas issuing from another glass tube, inserted into the other perforation of the cork, pass through one or two U tubes containing a neutral solution of nitrate of silver. When the flask is filled with carbonic acid, heat it gently on the water-bath. Continue the operation for several hours. If free phosphorus is present, it will volatilize unoxidized in the carbonic acid stream, then pass into the silver solution, where it will be partly converted into black phosphide of silver, partly into phosphoric acid. If no precipitate forms, you may safely conclude that no unoxidized phosphorus is present, whilst, on the other hand, the formation of a precipitate is not sufficient proof of the presence of phosphorus, as the precipitate may owe its formation to volatile reducing agents or to hydrosulphuric acid.

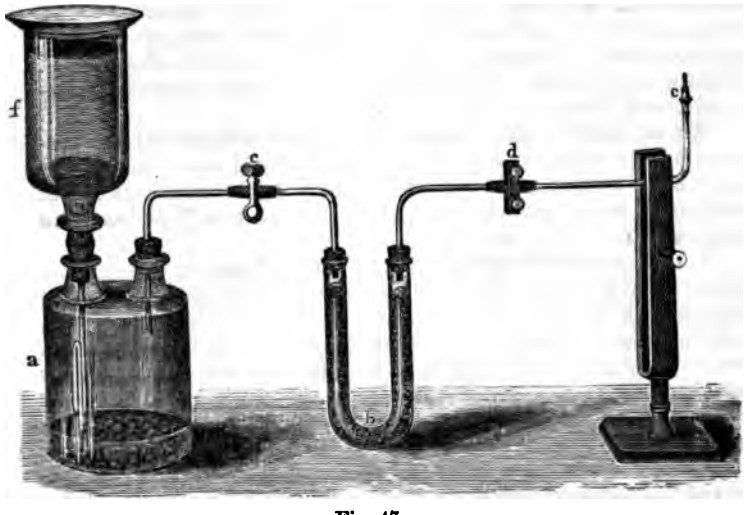


Fig. 47.

If a precipitate has formed, filter through a filter well washed **321** with dilute nitric acid and water, and wash. The presence of phos-

* In testing for hydrocyanic acid at the same time, it is best to collect the first 15 c.c. of the distillate separately, and to examine this for hydrocyanic acid, the subsequent portions for phosphorus.

phide of silver in it may be shown by BLONDLOT's improved modification of DUSSARD's method,* substituting, however, for the apparatus used by BLONDLOT, the one shown (fig. 47), which may be easily constructed.

*a* is a hydrogen-evolution bottle, *b* contains pumice-stone moistened with concentrated solution of potassa, *c* is a common clip, *d* a screw clip, *e* a platinum jet, which is kept cool by tying moistened cotton round it. This platinum jet is indispensable to the production of a colorless hydrogen flame, as the soda in the glass will always color the flame yellow.

To ascertain whether the zinc and sulphuric acid will give a gas quite free from phosphuretted hydrogen, let the evolution go on a short time, then close *c* until the fluid has ascended from *a* to *f*. Close *d*, open *c*, and regulate *d* by means of the screws so as to obtain a suitable flame. If the flame, viewed in a dark place, is colorless, showing no trace of a green cone in the centre, and no emerald-green coloration when pressed upon by a piece of porcelain, as in MARSH's experiment, the hydrogen may be considered pure. It is advisable to repeat the experiment. Rinse the precipitate under examination into *f*, take care that every particle of it reaches *a*, then repeat the experiment again. If the precipitate contains even a minute trace of phosphide of silver, the green cone in the centre of the flame and the emerald-green coloration will now become distinctly visible.

Remove the excess of silver from the solution filtered from the 322
silver precipitate, by hydrochloric acid, pass through a filter well washed with acid and water, remove the hydrochloric acid by evaporation on the water-bath, take up with nitric acid, and test for phosphoric acid with molybdate of ammonia, or with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia (NEUBAUER and FRESENIUS†).

We obtained by this method the clearest evidence of the presence of phosphorus in a large quantity of putrid blood mixed with the head of a common lucifer match; and this even in presence of substances which prevent the luminosity of the phosphorus in MITSCHERLICH's method.

5. If there is sufficient phosphorus present to permit a quanti- 323
tative determination, this may be effected by SCHERER's modification of MITSCHERLICH's method, viz., by distilling the mass, acidified with sulphuric acid, in an atmosphere of carbonic acid. I would suggest, with respect to this, to have the distilling flask furnished with a doubly perforated cork, and to transmit pure carbonic acid gas until the apparatus is filled with it, but then to shut off the carbonic acid stream. A flask with doubly perforated cork serves for receiver; the mouth of the condensing tube passes into one of the openings; into the other is inserted a bent glass-tube, which leads to a U tube containing a solution of pure nitrate of silver.

When the distillation is over, minute globules of phosphorus are found in the receiver. A moderate stream of carbonic acid is now once more transmitted through the apparatus, and a gentle

* Zeitschr. f. anal. Chem. 1, 129. † *Ibid.* 1, 336.

heat applied, with a view to effect the formation of larger globules by aggregation. These are then washed and weighed as in MITSCHERLICH'S method. The fluid poured off the phosphorus globules is luminous in the dark when shaken. It requires, however, a larger proportion of phosphorus to obtain distinct luminosity in this way than is the case with MITSCHERLICH'S method. The phosphorus in the fluid may, after oxidation by nitric acid or chlorine, be determined as phosphoric acid. However, the result is reliable only if the operation has been conducted with the requisite care to guard against the spirting over of portions of the boiling fluid, which often contains phosphoric acid. To obtain the remainder of the phosphorus, treat the contents of the U tube with nitric acid, throw down the silver by hydrochloric acid, filter through a washed filter, concentrate in a porcelain dish, precipitate the phosphoric acid as phosphate of magnesia and ammonia, and weigh it as pyrophosphate of magnesia.

B. *Detection of Phosphorous Acid.*

Should all attempts to detect phosphorus fail, try whether it 324
may not be practicable to find the first product of its oxidation, *i.e.*, phosphorous acid. For this purpose transfer the residue left in the distilling flask in **318** or in **323**, or the residue left in **320**, to the apparatus illustrated by fig. 47, having previously tested the purity of the zinc and sulphuric acid, then proceed according to the instruction of **321**, and observe whether the coloration of the hydrogen flame reveals the presence of phosphorus (WÖHLER). Should this be the case, the end in view is attained; if not, the presence of organic substances may be the preventive cause. If, therefore, the flame remains uncolored, shut the clip at once, connect with the apparatus a U tube containing solution of neutral nitrate of silver, open the clip again, and let the gas pass for many hours, in a slow stream, through the silver solution. If phosphorous acid is present, a precipitate containing phosphide of silver will separate in the silver solution; examine it according to **321**.*

3. *Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, &c.* (*Analysis of Ashes.*)

§ 228.

A. PREPARATION OF THE ASH.

It is sufficient for the purposes of a qualitative analysis to inci- 325
nerate a comparatively small quantity of the substance, which must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be conducted also in a Hessian crucible placed in a slanting position, or under certain circumstances, even in a porcelain or platinum dish, with the aid

* W. HERAPATH'S statement (Pharm. Journ. 1865, 573), that phosphoric acid is also reduced by zinc and dilute sulphuric acid, I have not found to be in accordance with the facts. Compare my paper in the Zeitschr. f. anal. Chem. 6, 203.

of a wide glass tube or lamp-glass, to increase the draught. The heat must always be moderate, to guard the volatilization of certain constituents, especially of chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as the ash of beet-root molasses, it is best, after thorough carbonization has been effected, to boil with water, and finally to incinerate the washed and dried residue. For further particulars see *Quantitative Analysis.*

## B. Examination of the Ash.

As the qualitative analysis of an ash is undertaken, either as 326
a practical exercise, or for the purpose of determining its general character, and the state in which any given constituent may happen to be present, or also with a view to make, as far as practicable, an approximate estimation of the quantities of the several constituents, it is usually the best way to examine separately, the part soluble in water, the part soluble in hydrochloric acid, and the residue which is insoluble in both. This can be done the more readily, as the number of bodies to be looked for is but small.

### *a. Examination of the Part soluble in Water.*

Boil the ash with water, filter, and whilst the residue is being washed, examine the solution as follows:—

1. Add to a portion, after heating it, hydrochloric acid in excess, 327
warm, and allow to stand. Effervescence indicates CARBONIC ACID combined with alkalies; smell of hydrosulphuric acid indicates the SULPHIDE OF AN ALKALI METAL, formed from an alkaline sulphate by the reducing action of the carbon. Turbidity from separation of sulphur, with smell of sulphurous acid, denotes a HYPOSULPHITE (which occurs occasionally in the ash of coal). Filter if necessary, and add chloride of barium to the fluid; a white precipitate indicates SULPHURIC ACID.

2. Evaporate another portion to a small volume, add hydro- 328
chloric acid to acid reaction (effervescence indicates CARBONIC ACID), test a few drops for BORACIC ACID with turmeric, evaporate to dryness, and treat the residue with hydrochloric acid and water; a residue consists of SILICIC ACID. Filter, add ammonia, chloride of ammonium, and sulphate of magnesia; a white precipitate indicates PHOSPHORIC ACID. Instead of this reaction, you may also mix the fluid filtered from the silicic acid with acetate of soda, and then cautiously add sesquichloride of iron, or you may evaporate with excess of nitric acid on the water-bath to dryness, treat the residue with nitric acid, and test with molybdate of ammonia (§ 142).

3. Add to another portion nitrate of silver as long as a precipi- 329
tate continues to form; warm gently, and then cautiously add ammonia; if a black residue is left, this consists of sulphide of silver, proceeding from the sulphide of an alkali metal, or from a hyposulphite. Filter if necessary, add nitric acid in slight excess, to effect the solution of the phosphate of silver precipitate formed,

leaving thus only CHLORIDE (iodide,* bromide) OF SILVER undissolved. Filter, and examine the precipitate as directed **178**, neutralize the filtrate exactly with ammonia. If this produces a light yellow precipitate, the phosphoric acid found in **328** was present in the tribasic, if a white precipitate, it was present in the bibasic form.

4. Heat a portion with hydrochloric acid, then make it alkaline **330** with ammonia; mix with oxalate of ammonia, and allow to stand. A white precipitate indicates LIME. Filter, and mix the filtrate with ammonia and phosphate of soda; a crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIA. (Magnesia is often found in distinctly appreciable, lime only in exceedingly minute quantity, even where alkaline carbonates and phosphates are present.)

5. For POTASSA and SODA examine as directed § 197. If magnesia is present, first neutralize with hydrochloric acid, and remove the magnesia as directed § 196, 2.

6. LITHIA, which is much more frequently found in ashes than has hitherto been believed, and OXIDE OF RUBIDIUM, which almost constantly accompanies potassa, may be most readily detected by the spectroscope in the residue consisting of the alkali salts.

*b. Examination of the Part soluble in Hydrochloric Acid.*

Warm the residue left undissolved by water with hydrochloric **331** acid†—effervescence indicates CARBONIC ACID combined with alkaline earths; evolution of chlorine denotes OXIDES OF MANGANESE. Evaporate to dryness with a few drops of sulphuric acid, heat a little more strongly to separate the SILICIC ACID, moisten the residue with hydrochloric acid and some nitric acid, add water, warm, and filter. Examine the precipitate for BARYTA and STRONTIA according to **255**. Examine the solution as follows.

1. Test a portion with hydrosulphuric acid. If this produces any other than a perfectly white precipitate, you must examine it in the usual way. (The ashes of plants occasionally contain COPPER; if the plant has been manured with excrements deodorized by nitrate of lead, they may contain LEAD, and so on.)

2. Mix a portion with carbonate of soda, as long as the precipitate **332** formed redissolves upon stirring; then add acetate of soda, and some acetic acid. This produces, in most cases, a white precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON, mixed occasionally with PHOSPHATE OF ALUMINA. Filter, wash the precipitate, heat it with pure potash, filter and test the filtrate for ALUMINA by acidifying with hydrochloric acid, adding ammonia and warming. If the filtrate is reddish, there is more iron present than corresponds to the phosphoric acid; if it is colorless, add sesquichloride of iron drop by drop till the fluid is reddish. (The quantity of the precipitate of phosphate of sesquioxide of iron here formed will give you some idea of the amount of PHOSPHORIC ACID present.) Boil, if

* To detect the iodine in aquatic plants, dip the plant in weak solution of potassa (CHATIN), dry, incinerate, treat with water, and examine the solution as directed (258).

† If the residue still contains much carbon after further incineration.

the fluid does not lose its color, add more acetate of soda and boil again, filter hot, neutralize the filtrate exactly with ammonia, mix with sulphide of ammonium in a flask, fill up the latter, close the mouth, allow to stand some time and filter. Test the precipitate according to **141** for MANGANESE and ZINC (the latter is seldom present); test the filtrate for LIME and MAGNESIA (**330**). The lime may contain a little STRONTIA and must therefore be tested according to p. 98.

3. Test the rest for, FLUORINE according to § 146, 6.

*c. Examination of the Residue insoluble in Hydrochloric Acid.*

The residue insoluble in hydrochloric acid contains,

1. The silicic acid, which has separated on treating with hydro- **333** chloric acid.

2. Those ingredients of the ash which are insoluble in hydrochloric acid. These are, in most ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stalk of cereals and others abounding in silicic acid that are not completely decomposed by hydrochloric acid.

Boil the washed residue with solution of carbonate of soda in **334** excess, filter hot, wash with boiling water, and test for silicic acid in the filtrate by evaporation with hydrochloric acid (§ 150, 2). If the ash was of a kind to be completely decomposed by hydrochloric acid, the analysis may be considered finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fusing. But if the ash abounded in silicic acid, and it may therefore be supposed that the hydrochloric acid has failed to effect complete decomposition, evaporate half of the residue insoluble in solution of carbonate of soda with pure solution of soda in excess, in a silver or platinum dish, to dryness. This decomposes the silicates of the ash, whilst but little affecting the sand. Acidify now with hydrochloric acid, evaporate to dryness, &c., and proceed as in **331**. For the detection of the alkalies use the other half of the residue, treating this according to **228**.

# SECTION III.

## EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

### I. Additional Remarks to the Preliminary Examination.

To §§ 175—178.

The inspection of the physical properties of a body may, as already stated, in many cases enable the analyst to draw certain general inferences as to its nature. Thus, for instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead &c. Inferences of this kind are quite admissible to a certain extent; but if carried too far, they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; however, the glass tube gives, in most cases, results more clearly evident, and affords moreover the advantage that volatile bodies are less likely to escape detection. To ascertain the products of oxidation of a body it is sometimes advisable also to heat it in a short glass tube, open at both ends, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means (§ 156, 6).

With respect to the preliminary examination by means of the blowpipe, I have to remark that the student must avoid drawing positive conclusions, until he has acquired some practice. A slight incrustation of the charcoal, which may seem to denote the presence of a certain metal, is not always a conclusive proof of the presence of that metal; nor would it be safe to assume the absence of a substance simply because the blowpipe flame fails to effect reduction, or solution of nitrate of protoxide of cobalt fails to impart a color to the ignited mass, &c. The blowpipe reactions are, indeed, in most cases, unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time and trouble is very erroneous.

### II. Additional Remarks to the Solution, etc., of Substances.

To §§ 179—181.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from sparingly soluble to insoluble is very gradual. Sulphate of lime, which is soluble in 430 parts of

water, might perhaps serve as a limit between the two classes, since this salt may still be positively detected in aqueous solution by the delicate reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon platinum foil, to see whether it holds a solid body in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance. In cases of the kind test, in the first place, the reaction of the fluid with litmus-papers; in the second place, add to a portion of it a drop of solution of chloride of barium; and lastly, to another portion some carbonate of soda. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not, as a general rule, examine it any further for bases or acids; since if the fluid contained any of those bases or acids which principally form sparingly soluble compounds, the chloride of barium and the carbonate of soda would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination, the student will always do well to examine the solution both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound and will give greater certainty—two advantages which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in hydrochloric acid or in nitric acid: the phosphates, arsenates, arsenites, borates, carbonates, and oxalates of the earths and metals; also several tartrates, citrates, malates, benzoates, and succinates; the oxides and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are, indeed, decomposed, if not by dilute, by boiling concentrated hydrochloric acid;* but this decomposition gives rise to the formation of insoluble compounds where oxide of silver is present, and of sparingly soluble compounds in the presence of suboxide of mercury and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid leaves a residue. On the other hand, however, nitric acid leaves, besides the bodies insoluble in any simple acid, teroxide of antimony, binoxide of tin, binoxide of lead, &c., undissolved, and dissolves many other substances less readily than hydrochloric acid—*e. g.*, sesquioxide of iron and alumina.

Substances not soluble in water are therefore, briefly, to be treated as follows: try to dissolve them in dilute or concentrated, cold or boiling hydrochloric acid; if this fails to effect complete solution, try to dissolve a fresh portion in nitric acid; if this also fails, treat the body with aqua regia, which is an excellent solvent, more particularly for metallic sulphides. To examine separately the solution in hydrochloric acid or in nitric acid, on the one hand, and that in nitrohydrochloric acid on the other, is, in most cases, neither necessary nor desirable. To prepare a solution in nitric acid or in aqua regia, where the nature of the substance

* For the exceptions see § 203.

does not absolutely demand it, is not advisable, as a solution in hydrochloric acid is much better suited for precipitation by hydrosulphuric acid. Nor is it advisable to concentrate a solution in aqua regia by evaporation, to drive off the excess of the acids, as the operation might lead to the escape of volatile chlorides, more particularly of chloride of arsenic. It is therefore always best to use no more aqua regia than is just necessary to effect solution. Solutions prepared with hydrochloric acid generally contain the metallic oxides in the same state of oxidation in which they were originally present (except suboxide of mercury, since subchloride of mercury by protracted boiling with hydrochloric acid, gradually decomposes into mercury and chloride of mercury). On the other hand solutions prepared with nitric acid or aqua regia, frequently contain the metallic oxides in a higher state of oxidation, thus, for instance, protoxide of iron, protoxide of tin, and arsenious acid are converted into sesquioxide of iron, binoxide of tin, and arsenic acid.

With regard to the solution of metals and alloys, I have to remark that, upon boiling them with nitric acid, white precipitates will frequently form, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water or not, before he concludes that they consist of tin or antimony.

## III. Additional Remarks to the Actual Examination.

### To §§ 182—204.

### A. General Review and Explanation of the Analytical Course.

#### *a.* Detection of the Bases.

The classification of the bases into groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Section III. The systematic course of analysis, from § 189 to § 198, is founded upon this classification of the bases; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests. Respecting the detection of the several bases individually, I refer the student to the recapitulations and remarks in §§ 88—135.

The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, HYDROSULPHURIC ACID, SULPHIDE OF AMMONIUM, and CARBONATE OF AMMONIA: this is likewise the order of succession in which they are applied. Sulphide of ammonium performs a double part.

Let us suppose we have in solution the whole of the bases, together with arsenious and arsenic acids, and also phosphate of lime—which latter may serve as a type for the salts of the alkaline earths soluble in acids and reprecipitated unaltered by ammonia.

Chlorine forms insoluble compounds only with silver and mercury; chloride of lead is sparingly soluble in water. The insoluble subchloride

of mercury corresponds to the suboxide of that metal. If, therefore, we add to our solution :

1. *Hydrochloric Acid,*

we remove from it the metallic oxides of the first division of the fifth group, viz., the whole of the OXIDE OF SILVER and the whole of the SUBOXIDE OF MERCURY. From concentrated solutions a portion of the LEAD may likewise precipitate as chloride ; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrosulphuric acid completely precipitates the oxides of the fifth and sixth groups from solutions containing a free mineral acid, since the affinity of the metallic radicals of these oxides for sulphur, and that of the hydrogen for oxygen, is sufficiently powerful to overcome the affinity between the metal and the oxygen, and that between the oxide and a strong acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under these circumstances, since those of the first and second groups form no sulphur compounds insoluble in water, besides their sulphides cannot possibly form in acid solutions; as regards those of the third group, sulphide of aluminium and sulphide of chromium cannot possibly be formed in the humid way; and the affinity which the metallic radicals of the oxides of the fourth group possess for sulphur, combined with that manifested by hydrogen for oxygen, is not sufficiently powerful to overcome the affinity of the metal for oxygen and of the oxide for a strong acid, IF THE LATTER IS PRESENT IN EXCESS.

If, therefore, after the removal of the oxide of silver and suboxide of mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrosulphuric Acid,*

we remove from it the remainder of the oxides of the fifth, together with those of the sixth group, viz., OXIDE OF LEAD, OXIDE OF MERCURY, OXIDE OF COPPER, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE OF ANTIMONY, ARSENIOUS ACID, and ARSENIC ACID. All the other oxides remain in solution, either unaltered, or reduced to a lower degree of oxidation, *e. g.*, sesquioxide of iron, chromic acid, &c.

The sulphides (at least the higher sulphides) corresponding to the oxides of the sixth group combine with basic metallic sulphides (the sulphides of the alkali metals), and form with them sulphur salts soluble in water; while the sulphides corresponding to the oxides of the fifth group do not possess this property, or possess it only to a limited extent.* If, therefore, we treat the whole of the sulphides precipitated by hydrosulphuric acid from an acid solution, with—

3. *Sulphide of Ammonium* (or, in certain cases, *Sulphide of Sodium*),

with addition, if necessary, of some sulphur or yellow sulphide of ammonium, the sulphides of mercury, lead, copper, bismuth, and cadmium remain undissolved, whilst the other sulphides dissolve as double com-

* Sulphide of mercury combines with sulphide of potassium and sulphide of sodium, but not with sulphide of ammonium ; sulphide of copper dissolves a little in sulphide of ammonium, but not in sulphide of potassium or sulphide of sodium.

pounds of sulphide of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with sulphide of ammonium (or, as the case may be, sulphide of sodium), and precipitate again from this solution upon the addition of hydrochloric acid, either unaltered, or in a state of higher sulphuration (they take up sulphur from the yellow sulphide of ammonium). The rationale of this precipitation is as follows :—The acid decomposes the sulphur salt formed. The sulphur base (sulphide of ammonium or sulphide of sodium) is decomposed by the hydrochloric acid into chloride and hydrosulphuric acid; and the liberated sulphur acid precipitates. Sulphur precipitates at the same time if the sulphide of ammonium contains an excess of that element. The analyst must bear in mind that this eliminated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The sulphides corresponding to the oxides still remaining in solution are part of them—as those of the alkalies and alkaline earths—soluble in water; part—as those of alumina and sesquioxide of chromium—decomposed by water into hydrated oxides and hydrosulphuric acid; part—as those of the fourth group—insoluble in water. These latter would accordingly have been precipitated by hydrosulphuric acid, but for the free acid present. If, therefore, this free acid is removed, *i.e.*, if the solution is made alkaline, and then treated with more hydrosulphuric acid, if required, or, what will answer both purposes at once, if

4. *Sulphide of Ammonium,*

is added to the solution,* the sulphides corresponding to the oxides of the fourth group will precipitate : viz., the SULPHIDES OF IRON, MANGANESE, COBALT, NICKEL, and ZINC. But in conjunction with them, HYDRATE OF ALUMINA, HYDRATED SESQUIOXIDE OF CHROMIUM, and PHOSPHATE OF LIME are thrown down, because the affinity which the oxide of ammonium possesses for the acid of the salt of alumina or of sesquioxide of chromium, or for that which keeps the phosphate of lime in solution, causes the elements of the sulphide of ammonium to transpose with those of the water, thus giving rise to the formation of oxide of ammonium and of hydrosulphuric acid. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides or with the phosphate of lime,—the oxides and the lime-salt precipitate.

There remain now in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water, whilst those of the latter are soluble. If, therefore, we now add

5. *Carbonate of Ammonia,*

together with a little pure ammonia, to guard against the possible formation of bicarbonates, the whole of the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTA, STRONTIA, and LIME;† of magnesia we know that, owing to its disposition to form

* After previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrosulphuric acid : and after previous addition also, if necessary, of chloride of ammonium to prevent the precipitation of magnesia by ammonia.

† It has been already mentioned in § 99 that traces of these remain in solution partly because their carbonates are not absolutely insoluble in water, but principally because they are notably soluble in chloride of ammonium. On account of this deportment we test the filtrate from the carbonate of ammonia precipitate with sulphate and oxalate of ammonia (164). In the general explanation of the course given in the text, these traces of baryta, strontia, and lime are not taken into account.

double compounds with salts of ammonia, it precipitates only in part; and that the presence of an additional salt of ammonia will altogether prevent its precipitation, at least within a reasonable space of time. To guard against any uncertainty arising from this cause, chloride of ammonium is added previously to the addition of the carbonate of ammonia, the mixture soon after filtered, and thus the precipitation of the magnesia is altogether prevented.

We have now still in solution MAGNESIA and the ALKALIES. The detection of magnesia may be effected by means of phosphate of soda and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of that earth in the pure state. The substance under examination is accordingly ignited in order to expel the salts of ammonia, and the magnesia is then precipitated by means of baryta, the alkalies, together with the newly formed salt of baryta and the excess of the caustic baryta added, remaining in solution. By the addition of carbonate of ammonia the compounds of baryta are removed from the solution, which now only contains the fixed alkalies, the salt of ammonia formed, and the excess of the salt of ammonia added. If the salts of ammonia are then removed by ignition, the residue consists of the fixed alkalies alone. But as carbonate of baryta is slightly soluble in salts of ammonia, and gives upon evaporation with chloride of ammonium, carbonate of ammonia and chloride of barium, it is usually necessary, after the expulsion of the salts of ammonia by ignition, to precipitate once more with carbonate of ammonia and a few drops of oxalate of ammonia, in order to obtain a solution perfectly free from baryta.

Lastly, to effect the detection of the AMMONIA, a fresh portion of the substance must of course be taken.

### *b.* Detection of the Acids.

Before passing on to the examination for acids and salt-radicals, the analyst should first ask himself which of these substances may be expected to be present, to judge from the nature of the detected bases and the class to which the substance under examination belongs with respect to its solubility, since this will save him the trouble of unnecessary experiments. Upon this point I refer the student to the table in Appendix IV.

The general reagents applied for the detection of the acids are, for the inorganic acids, CHLORIDE OF BARIUM and NITRATE OF SILVER, for the organic acids CHLORIDE OF CALCIUM and SESQUICHLORIDE OF IRON. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether the presence of organic acids must also be looked for. The latter is invariably the case if the body, when ignited, turns black, owing to separation of carbon. In the examination for bases the general reagents serve to effect the actual separation of the several groups of bases from each other; but in the examination for acids they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids, in combination with soda, for instance

Baryta forms insoluble, or difficultly soluble, compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; fluoride of barium also is insoluble, or at least only sparingly soluble; all these compounds are soluble in hydrochloric acid, with the exception of sulphate of baryta. If, therefore, to a portion of our neutral or, if necessary, neutralized solution, we add,

1. *Chloride of Barium,*

the formation of a precipitate will denote the presence of at least one of these acids. By treating the precipitate with hydrochloric acid we learn at once whether sulphuric acid is present or not, as all the salts of baryta being soluble in this menstruum, with the exception of the sulphate, a residue left undissolved by the hydrochloric acid can consist only of the latter salt. Where sulphate of baryta is present, the reaction with chloride of barium fails to lead to the positive detection of the whole of the other acids enumerated; for upon filtering the hydrochloric solution of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not always fall down again, being kept in solution by the chloride of ammonium formed. For this reason chloride of barium cannot serve to effect the actual separation of the whole of the acids named, and, except as regards sulphuric acid, we set no value upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, since the non-formation of a precipitate upon its application in neutral or alkaline solutions proves at once the absence of so considerable a number of acids.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferro- and ferricyanogen, and of the oxide of silver with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble, or difficultly soluble, in water. The whole of these compounds are soluble in dilute nitric acid, with the exception of the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, and sulphide of silver. If, therefore, we add to our solution, which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of Silver,*

and precipitation ensues, this shows at once the presence of one or several of the acids enumerated: chromic acid, arsenic acid, and several others, which form colored salts with silver, may be individually recognised with tolerable certainty by the mere color of the precipitate. By treating the precipitate now with nitric acid, we see whether it contains sulphide of silver or any of the haloid compounds of silver, as these remain undissolved, whilst all the oxide salts dissolve. Nitrate of silver fails to effect the complete separation of those acids which form with oxide of silver compounds insoluble in water, from the same cause which renders the separation of acids by chloride of barium uncertain, viz., the ammoniacal salt formed prevents the reprecipitation, by ammonia, of several of the salts of silver from the acid solution. Nitrate of silver, besides effecting the separation of chlorine, iodine, bromine, cyanogen, &c., and indicating the presence of chromic acid, &c., serves, like the

chloride of barium, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with chloride of barium and with nitrate of silver, indicates therefore at once the further course of the investigation. Thus, for instance, where chloride of barium has produced a precipitate, whilst nitrate of silver has failed to do so, it is not necessary to test for phosphoric acid, chromic acid, boracic acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always the solution was sufficiently concentrated and did not already contain salts of ammonia. The same is the case if we obtain a precipitate by nitrate of silver, but none by chloride of barium.

Returning now to the supposition which we have made here, viz., that the whole of the acids are present in the solution under examination, the reactions with chloride of barium and nitrate of silver would accordingly have demonstrated already the presence of SULPHURIC ACID, and led to the application of the special tests for CHLORINE, BROMINE, IODINE, CYANOGEN, FERROCYANOGEN, FERRICYANOGEN, and SULPHUR;* and there would be reason to test for all the other acids precipitable by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, accordingly to nitric acid and chloric acid.

Of the ORGANIC ACIDS, oxalic acid, paratartaric acid, and tartaric acid, are precipitated by chloride of calcium in the cold, in presence of chloride of ammonium; the two former immediately, the latter often only after some time; but the precipitation of citrate of lime is prevented by the presence of salts of ammonia, and ensues only upon ebullition or upon mixing the solution with alcohol; the latter agent serves also to effect the separation of malate and succinate of lime from aqueous solutions. If, therefore, we add to our fluid,—

3. *Chloride of Calcium in excess* and Chloride of Ammonium,

OXALIC ACID, PARATARTARIC ACID, and TARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, phosphate of lime for instance, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids such reactions only as preclude the possibility of confounding the organic acids with the inorganic acids that are thrown down along with them. For the detection of oxalic acid we select accordingly solution of sulphate of lime, with acetic acid (§ 145); to effect the detection of the tartaric and paratartaric acids, we treat the precipitate produced by chloride of calcium with solution of soda, since the lime-salts of these two acids only are soluble in this menstruum in the cold, but insoluble upon ebullition.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID, MALIC ACID, and SUCCINIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, &c., of lime, which still contains an excess of chloride of calcium. Sulphate and

* For the separation and special detection of these substances, I refer to § 157.

borate of lime invariably precipitate along with the malate, citrate, and succinate of lime, if sulphuric acid and boracic acid happen to be present; the analyst must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid, malic acid, and succinic acid. The alcohol is now removed by evaporation, and—

4. *Sesquichloride of Iron*

added to the perfectly neutral fluid. This reagent precipitates the BENZOIC ACID and the rest of the SUCCINIC ACID in combination with sesquioxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from each other, and the reactions on which the individual detection of the various acids is based, have been fully described and explained in the former part of this work.

## B. Special Remarks and Additions to the Systematic Course of Analysis.

I will here call attention to several matters which were necessarily passed over in the description of the ordinary course of analysis, and I shall take the present opportunity of explaining how the course may be expanded to meet the detection of the RARE METALS.

### To § 189.

At the commencement of § 189 the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group by hydrosulphuric acid. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration that nitric acid also produces precipitates in many cases—in a solution of potassio-tartrate of antimony, for instance—I prefer the use of hydrochloric acid, *i.e.*, the complete precipitation by that acid of all that is precipitable by it, for the following reasons: 1. Metals are more readily precipitated by hydrosulphuric acid from solutions acidified with hydrochloric acid, than from those acidified with nitric acid; 2. In cases where the solution contains silver, suboxide of mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these three metals in the form of chlorides; and 3. This latter form is the best adapted for the individual detection of these three metals when present in the same solution. Besides, the application of hydrochloric acid saves the necessity of examining whether the mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the form of oxide or in that of suboxide. That the lead, if present in large proportion, is obtained partly in the form of a chloride, and partly in the precipitate produced by hydrosulphuric acid in the acid solution, can hardly be thought an objection to the application of this method, as the removal of the larger portion of the lead from the solution, effected at the commencement, will only serve to facilitate the examination for other metals of the fifth and sixth groups.

As already remarked, a basic salt of teroxide of antimony may separate from potassio-tartrate of antimony, for instance, or from some other analogous compound, and precipitate along with the insoluble chloride of silver and subchloride of mercury, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated subchloride of mercury into chloride.

Should bismuth, antimony, or metastannic acid be present, the addition of the washings of the precipitate produced by hydrochloric acid to the first filtrate will cause turbidity. The turbidity is occasioned, in the case of bismuth and antimony, by the insufficiency of the free hydrochloric acid present to prevent the separation of basic salt, in the case of metastannic acid, by the metastannic chloride being first precipitated, then redissolving in the wash water, and then meeting with hydrochloric acid in the filtrate. This turbidity exercises, however, no influence upon the further process, since hydrosulphuric acid as readily converts these finely-divided precipitates into sulphides as if the metals were in actual solution.

In the case of alkaline solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction combines with the hydrochloric acid, and the bodies originally dissolved in that alkaline substance separate. Thus, if the alkali is present in the free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides will redissolve in an excess of hydrochloric acid, whereas chloride of silver will not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt is the cause of the alkaline reaction, the sulphur acid, *e. g.*, tersulphide of antimony, precipitates upon the addition of the hydrochloric acid, whilst the sulphur base, *e. g.*, sulphide of sodium, transposes with the constituents of the hydrochloric acid, forming chloride of sodium and hydrosulphuric acid. If an alkaline carbonate, a cyanide, or the sulphide of an alkali metal is the cause of the alkaline reaction, carbonic acid, or hydrocyanic acid, or hydrosulphuric acid escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of entire groups of bodies.

Precipitates are produced also by hydrochloric acid in solutions containing thallium, alkali salts of antimonic acid, tantalic acid, niobic acid, molybdic acid, and tungstic acid. The antimonic, tantalic, and molybdic precipitates dissolve (the tantalic acid precipitate to an opalescent fluid), whilst the CHLORIDE OF THALLIUM, NIOBIC ACID, and TUNGSTIC ACID do not dissolve in excess of hydrochloric acid. The latter therefore remain with the precipitate, which may also contain chloride of silver, subchloride of mercury, chloride of lead, and silicic acid. Separation of sulphur ensuing after some time on addition of hydrochloric acid, accompanied by the odor of sulphurous acid indicates HYPOSULPHUROUS ACID. If you have cause to test for rare metals, after exhausting the precipitate with boiling water, examine the fluid for THALLIUM by iodide of potassium (confirming by the spectroscope). On exhausting again with ammonia to dissolve out the chloride of silver, and treating the residue with nitric acid, the niobic, tungstic, and silicic acids will remain behind. The two first may be separated from the latter by fusing with bisulphate of potassa, treating with water, and finally with dilute solution of carbonate of ammonia. They may be separated from each other by treating the solution with excess of sulphide of ammonium.

## To §§ 190 and 191.

A judicious distribution and economy of time is especially to be studied in the practice of analysis; many of the operations may be carried on simultaneously, which the student may readily perceive and arrange for himself. For instance, after throwing the hydrosulphuric acid precipitate on the filter, you may test the first drops of the filtrate with sulphide of ammonium to see if there is any metal of that group present, and if this is not the case you may proceed to test with carbonate of ammonia. You will thus be able, while washing the hydrosulphuric acid precipitate, to throw down the filtrate with the proper group test. Again, while you are treating the first precipitate with sulphide of ammonium you may wash the second precipitate.

In cases where the analyst has simply to deal with metallic oxides of the sixth group (*e. g.*, teroxide of antimony) and of the fourth or fifth group (*e.g.*, iron or bismuth), he need not precipitate the acidified solution with hydrosulphuric acid, but may, after neutralization, at once add sulphide of ammonium in excess. The sulphide of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in solution, from which they will, by addition of an acid, at once be thrown down as tersulphide of antimony, &c. This method has the advantage that the fluid is diluted less than is the case where solution of hydrosulphuric acid is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrosulphuric acid gas is conducted into the fluid. I must again call attention to the very constant occurrence of mistakes through the use of spoilt hydrosulphuric acid water, through the use of an insufficient quantity of good hydrosulphuric acid water, or through passing the gas into a solution containing a too large excess of hydrochloric or nitric acid. Imagine a very acid solution containing iron and bismuth; if you pass hydrosulphuric acid gas or add a few drops of the water, no precipitate will be produced; and if in the idea that no metal of the hydrosulphuric acid group is present, you then add sulphide of ammonium, you will obtain a precipitate containing the sulphides of iron and bismuth; and on treating this with dilute hydrochloric acid, the sulphide of bismuth will remain as a black residue indicating the presence of nickel or cobalt. In this case you should have either diluted the fluid considerably before passing the gas, or added a large quantity of hydrosulphuric acid water; when the bismuth would have been precipitated in its proper place. Again, arsenic acid may be easily missed if the action of the hydrosulphuric acid is not supplemented by heat.

If the hydrosulphuric acid precipitate is not well washed, on warming it with nitric acid the sulphide of mercury may dissolve from the presence of hydrochloric acid, and on testing the action of sulphide of ammonium the results will not be trustworthy.

It happens occasionally that in treating acid solutions with hydrosulphuric acid, or in decomposing by hydrochloric acid the sulphide of ammonium used to effect the solution of sulphides of the sixth group that may be present, precipitates are obtained which look almost like pure sulphur, and thus leave the analyst in doubt whether it is really requisite to examine them for metals. In such cases the precipitate may be first washed, then dried, and treated finally with sulphide of carbon;

to remove the sulphur; this will show whether or not a trifling quantity of a sulphide is mixed with the sulphur.

The following sulphides of the rarer elements pass into the precipitate produced by hydrosulphuric acid in an acid solution; the sulphides of palladium, rhodium, osmium, ruthenium, iridium,* molybdenum, tellurium, selenium, and possibly of thallium.†

The following rare compounds cause separation of sulphur, by decomposing the hydrosulphuric acid; the higher oxides and chlorides of manganese and cobalt, vanadic acid (with blue coloration of the fluid), nitrous acid, sulphurous acid, hyposulphurous acid, hypochlorous and chlorous acids, bromic acid, and iodic acid.

On treating the precipitate with sulphide of ammonium (sulphide of sodium), the sulphides of iridium, molybdenum, tellurium, and selenium dissolve, whilst the sulphides of palladium, rhodium, osmium, and ruthenium, and of thallium, remain undissolved.

### To § 192.

If a precipitate containing all the sulphides of the sixth group, precipitable by hydrosulphuric acid, from acid solution, (of tin, antimony, arsenic, tellurium, selenium, molybdenum, gold, platinum, and iridium) is fused, according to § 192, with carbonate and nitrate of soda, and the fused mass treated with cold water, the TELLURIC ACID, SELENIC ACID, and MOLYBDIC ACID dissolve with the arsenic acid, whilst the IRIDIUM is left undissolved with the binoxide of tin, antimonate of soda, gold, and platinum.

For the way of detecting the rare elements in the solution and in the precipitate, see § 135.

### To § 193.

Besides the methods described in the systematic course, to separate cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results. Add carbonate of soda to the nitric acid solution as long as a precipitate continues to form, then solution of cyanide of potassium in excess, and heat gently. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution in the form of cyanide of copper and potassium, and cyanide of cadmium and potassium. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, hydrosulphuric acid in excess, gently heating, and then adding some more cyanide of potassium, in order to redissolve the sulphide of copper which may have precipitated along with the sulphide of cadmium. A residuary yellow precipitate (sulphide of cadmium), insoluble in the cyanide of potassium, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (sulphide of copper) will demonstrate the presence of copper.

Where there is reason to suppose that the precipitate containing the sulphides of the fifth group contains also the sulphides of palladium, rhodium, osmium, ruthenium, or thallium, first test a portion in the spectroscope for thallium, and then proceed as follows:

Fuse the precipitate with hydrate of potassa and chlorate of potassa, heat, ultimately

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* The metals of the platinum ores are precipitated with difficulty by hydrosulphuric acid. To attain the end in view, hydrosulphuric acid gas must be perseveringly conducted into the fluid, and heat applied at the same time.

† Tungsten and vanadium are not found in the precipitate thrown down from an acid solution by hydrosulphuric acid. They can be present only where the fluid has first been mixed with sulphide of ammonium, then with acid in excess; but in that case the sulphides of nickel and cobalt will also be found with those of the fifth and sixth groups. Thallium, although it is not precipitated from acid solutions by hydrosulphuric acid under ordinary circumstances, may be thrown down in combination with sulphide of arsenic.

to redness, let cool, then treat the mass with water. The solution contains osmate and ruthenate of potassa, which latter imparts a deep yellow color to it. If the fluid is cautiously neutralized with nitric acid, BLACK SESQUIOXIDE OF RUTHENIUM separates; if more nitric acid is added to the filtrate, and the fluid then distilled, OSMIC ACID passes over. If the residue left upon the extraction of the fused mass with water is gently ignited in hydrogen gas,* then cautiously treated with dilute nitric acid, the copper, lead, &c., are dissolved, whilst the rhodium and palladium are left undissolved. The PALLADIUM may then be dissolved out of the residue by means of aqua regia, leaving the RHODIUM undissolved. For the further examination of the isolated metals, I refer to § 124. A separate portion of the precipitate of the sulphides must be examined for mercury, in the event of the above process being adopted.

To § 194.

Assuming all elements not yet precipitated to be present in the fluid filtered from the precipitate produced in an acid solution by hydrosulphuric acid, the precipitate produced by addition of chloride of ammonium to this filtrate, neutralization with ammonia, and addition of sulphide of ammonium in excess, will contain the following elements:

*a.* In the form of sulphides: cobalt, nickel, manganese, iron, zinc, uranium, thallium, indium;

*b.* In the form of oxides: aluminium, beryllium, thorium, zirconium, yttrium, erbium, cerium, lanthanium, didymium, chromium, titanium, tantalum, niobium.†

Where there is reason to suspect the presence of some of the rare elements in the precipitate, the following method may be recommended as the most suitable in many cases:

1. Dry the greater part of the washed precipitate, ignite in a porcelain crucible, then fuse perseveringly in a platinum crucible with *acid sulphate of potassa;* let the fused mass cool, soak in cold water, and digest for some time without application of heat. Filter the solution from the residue.

The RESIDUE, which contains the acids of tantalum and niobium, and may contain also silicic acid and a little undissolved sesquioxide of iron and sesquioxide of chromium, gives, on fusion with hydrate of soda, and some nitrate of soda, a mass out of which dilute solution of soda will dissolve chromate and silicate of potassa, leaving undissolved, with the sesquioxide of iron, tantalate and niobate of soda (being insoluble in solution of soda). After removing the excess of soda, treat repeatedly with a very dilute solution of carbonate of soda, in which the NIOBATE of soda dissolves much more readily than the TANTALATE. For the further examination compare § 104, 10 and 11.

Treat the SOLUTION, which contains all the other bases, &c., of the third and fourth groups, with hydrosulphuric acid, to reduce the sesquioxide of iron, dilute considerably, heat to boiling, and keep boiling for some time, whilst conducting carbonic acid into the fluid. If a precipitate is formed, examine this for TITANIC ACID; it may possibly contain also a little ZIRCONIA.

Concentrate the filtrate by evaporation, with addition of some nitric acid; precipitate with *ammonia*, filter, and wash; redissolve the washed precipitate in hydrochloric acid, and precipitate again with ammonia. This will give almost the whole of the ZINC, MANGANESE, NICKEL, and COBALT in solution, whilst the earths are left undissolved with the oxides of iron, indium, uranium, and chromium. Redissolve the precipitate in hydrochloric acid, and add *concentrated solution of potassa*, without applying heat. This will leave in solution the sesquioxide of chromium, the alumina, and the berylla whilst precipitating the other earths with the oxides of iron, indium, and uranium. Dilute the alkaline solution, and boil some time; this will throw down the berylla, and the sesquioxide of chromium, leaving the ALUMINA in solution. The latter earth may then be precipitated by chloride of ammonium. Fuse the precipitate of berylla and sesquioxide of chromium with carbonate of soda and chlorate of potassa, and separate the BERYLLA from the CHROMIC ACID in the same way in which the separation of alumina from chromic acid is effected (§ 103).

The precipitate, which contains the oxides of iron, indium, and uranium, and the earths insoluble in potassa, may also contain oxide of chromium, and under certain circumstances, *e. g.*, in presence of yttria and sesquioxide of cerium, also alumina and berylla.

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* Cadmium may escape in this operation.

† Of niobic acid only the trifling traces redissolved on the precipitation by hydrochloric acid can be present here.

Dissolve it in hydrochloric acid, remove an over-large excess of the acid by evaporation, dilute, add *carbonate of baryta*, and let the mixture stand from four to six hours in the cold.

The precipitate produced contains the SESQUIOXIDE OF IRON, OXIDE OF INDIUM, and possibly ALUMINA, sesquioxide of chromium, and SESQUIOXIDE OF URANIUM. Separate the latter in a portion of the precipitate by redissolving in hydrochloric acid, and adding excess of bicarbonate of soda. Test another portion in the spectroscope for INDIUM, and another by fusing with carbonate of soda and chlorate of potassa for CHROMIUM.

To the filtrate from the carbonate of baryta precipitate, first add sulphuric acid to remove baryta, filter, concentrate strongly by evaporation, neutralize exactly with potassa (leaving the reaction rather acid than alkaline), add *neutral sulphate of potassa* in crystals, boil, and let the fluid stand twelve hours. Then filter, and wash with a solution of neutral sulphate of potassa. The filtrate contains that portion of the beryllia which may have escaped solution by potassa, also yttria and oxide of erbium. These substances are precipitated by ammonia, and may then easily be separated by treating with a concentrated warm solution of *oxalic acid*, in which the BERYLLA is soluble, whilst the oxalates of YTTRIA, and of OXIDE OF ERBIUM, are left undissolved. Now boil the precipitate of the double sulphates repeatedly in water, with addition of some hydrochloric acid, which will dissolve the THORIA and the OXIDES OF CERIUM, leaving the sulphate of ZIRCONIA and potassa undissolved. The thoria and the oxides of cerium may then be precipitated from the solution by ammonia, and tested by the reactions described in § 104.

2. Test a portion of the remainder of the precipitate in the spectroscope for THALLIUM (and also indium). To be more sure about thallium, dissolve a portion of the precipitate in boiling dilute hydrochloric acid, treat with sulphurous acid till sesquioxide of iron is reduced, nearly neutralize with ammonia, and then test with iodide of potassium. The precipitate must, under all circumstances, be further examined in the spectroscope.

To §§ 195—198.

The fluid filtered from the precipitate produced by sulphide of ammonium may not only contain the alkaline earths and the alkalies, but some nickel, and also vanadic acid and that portion of the tungstic acid which has been left unprecipitated by hydrochloric acid. The nickel, the vanadic acid, and the tungstic acid, are present as sulphides dissolved in the excess of sulphide of ammonium; they are thrown down in that form by just acidifying the fluid with hydrochloric acid. Filter the precipitate, wash, dry, fuse with carbonate of soda and nitrate of potassa, and treat the fused mass with water; this will dissolve the vanadate and tungstate of potassa, leaving the protoxide of nickel undissolved. From this solution the vanadic acid may be separated by means of solid chloride of ammonium, the tungstic acid by evaporating with hydrochloric acid and treating the residue with water. The two acids may then be examined as directed § 113, *d*, and § 13 , *c*.

For the detection of lithium, cæsium, and rubidium, I refer to the analysis of mineral waters (**259** and **260**).

To § 203.

If the rare elements are taken into account, the number of bodies which may remain undissolved on treating a substance with water, hydrochloric acid, nitric acid, and aqua regia, is much enlarged. The following bodies, more especially, are either generally, or in the ignited state, or in certain combinations, insoluble or slowly and sparingly soluble in acids:

Beryllia, thoria, and zirconia, sesquioxide of cerium, titanic acid, tantalic acid, niobic acid, molybdic acid, tungstic acid, rhodium, iridium, osmio-iridium, ruthenium.

When you have, in the systematic course of analysis, arrived at **208**, fuse the substance, free from silver, lead, and sulphur, with carbonate of soda and some nitrate of potassa, extract the fused mass repeatedly with hot water, and, if a residue is left, fuse this some time, in a silver crucible, with hydrate of potassa and nitrate of potassa, and again treat the fused mass repeatedly with water. The alkaline solutions, which may be examined separately or together, may contain beryllia, a portion of the titanic acid, tantalic acid, niobic acid, molybdic acid, tungstic acid, osmic and ruthenic acids, and a portion of the iridium.

If the residue left undissolved by the preceding operation is fused with acid sulphate of potassa, and the fused mass treated with water, the thoria, zirconia, and sesquioxide of cerium, the remainder of the titanic acid and the rhodium will dissolve. A residue left by this operation may consist of platinum ore metals, and had best be mixed with chloride of sodium, and ignited in a stream of chlorine.

With respect to the separation and detection of the several elements that have passed into the different solutions, the requisite directions and instructions have been given in the third section of Part I., and in the additional remarks to §§ 189–198.

## To § 204.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes a difficult task even to ascertain whether we have really a cyanide before us or not. However, if the reactions of the substance upon ignition (8) be carefully observed, and also whether upon boiling with hydrochloric acid any odor of hydrocyanic acid is emitted (35), the presence or absence of a cyanide will generally not remain a matter of doubt.

It must above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes, viz., they are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other analogous compound radical.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, &c., to which indeed the method described § 204 more exclusively refers, suffer by acids such complicated decompositions that their analysis by means of acids is a task not so easily accomplished. Their decomposition by potassa or soda is far more simple. The alkali yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide thus formed precipitates, and the reduced potassium or sodium forms with the liberated radical soluble ferrocyanide, &c., of potassium or sodium. But several oxides are soluble in an excess of potassa, as, *e.g.*, oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, is boiled with solution of caustic potassa, it dissolves completely, and we may assume that the solution contains ferrocyanide of potassium and oxide of zinc dissolved in potassa. Were we to add an acid to this solution, we should of course simply re-obtain the original precipitate of the double ferrocyanide of zinc and potassium, and the experiment would consequently be of no avail. To prevent this failure, we conduct hydrosulphuric acid into the solution in potassa, but only until the precipitable oxides are completely thrown down, and not until the solution smells of sulphuretted hydrogen. This serves to convert into sulphides all the heavy metals which the potassa holds in solution as oxides. Those sulphides which are insoluble in potassa, such as sulphide of lead, sulphide of zinc, &c., precipitate, whilst those which are soluble in alkaline sulphides, such as bisulphide of tin, tersulphide of antimony, &c., remain in solution. To effect the detection of these also, the fluid is now acidified and, if necessary, more hydrosulphuric acid conducted into it.

In the filtrate from the oxides and sulphides we have still those metals which form compound radicals with cyanogen, and also alumina, which has dissolved in the original treatment with potash, and would not have been separated. Finally also the other acids must be tested for here. It is therefore directed to divide the solution into two parts, and to test one for acids, the other for alumina and those metals which form compound radicals with cyanogen. The prescribed heating of this second part with concentrated sulphuric acid has the effect of decompos-

ing the cyanogen compounds, and converting the metals into sulphates which remain behind (H. Rose*).

If you simply wish to examine for bases in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, it will suffice to heat the powdered substance in a platinum dish with concentrated sulphuric acid diluted with a little water, till almost all the free acid is driven off. The residue will consist of sulphates which are to be dissolved in hydrochloric acid and water.

The reason why ferrocyanides and similar compounds which have been fully washed with water, require to be tested for alkalies is because alkaline ferrocyanides, &c., are often precipitated along with insoluble ferrocyanides, &c., and cannot be removed by washing.

* Zeitschr. f. anal. Chem. 1, 194.

# APPENDIX.

## I.

### Deportment of the most important Medicinal Alkaloids with Reagents, and Systematic Method of effecting their Detection.

§ 229.

The detection and separation of the alkaloids is far more difficult than the detection and separation of the inorganic bases. In many cases the combinations in which an alkaloid can be separated from others are not sufficiently insoluble to allow of an actual separation, in other cases we only know the outward appearance of a reaction and not its cause, and are consequently ignorant of the conditions which may modify its action; again, many alkaloids may be said to have no characteristic reaction whatever.

However, in the following pages the subject will be treated as thoroughly as our knowledge will allow, the more commonly occurring alkaloids being included, viz., nicotine, conine, morphine, narcotine, quinine, cinchonine, strychnine, brucine, veratrine, and atropine.

This appendix will be divided into the following sections:

A. General reagents for the alkaloids.

B. Properties and reactions of the individual alkaloids, arranged in groups. (In this section certain non-nitrogenous bodies are included which are allied to the alkaloids as poisons or are employed in their adulteration, namely, salicine, digitaline, and picrotoxine.)

C. Systematic course for the detection of an alkaloid when only one is present.

D. Systematic course for the detection of alkaloids when several may be present.

E. Detection of alkaloids in the presence of other organic substances.

### A. General Reagents for the Alkaloids.

§ 230.

By general reagents for the alkaloids I mean reagents by which they are all or nearly all precipitated. These are well suited to test generally for the presence of an alkaloid in a fluid, and may serve to separate alkaloids from their solutions, but they cannot be employed to distinguish individual alkaloids except in a subordinate degree.

These reagents are as follows: bichloride of platinum, a solution of iodine in iodide of potassium (Wagner*), double iodide of mercury and potassium (v. Planta†), double iodide of cadmium and potassium

* Zeitschr. f. anal. Chem. 4, 387.

† His Verhalten der wichtigsten Alkaloide gegen Reagentien, Heidelberg, 1846.

(MARME*), double iodide of bismuth and potassium (DRAGENDORFF†), phosphomolybdic acid (DE VRIJ, SONNENSCHEIN‡), phosphoantimonic acid (FR. SCHULZE§), metatungstic acid (SCHEIBLER‖), picric acid (H. HAGER¶).

BICHLORIDE OF PLATINUM forms with the hydrochlorates of the alkaloids compounds analogous to the ammonio-bichloride of platinum. Some of these compounds are difficultly soluble in water, some are rather easily soluble. They are best obtained and most completely separated by mixing the solutions with a sufficient quantity of bichloride of platinum, evaporating nearly to dryness and treating with alcohol. They have a yellow color of various shades, some are crystalline, some flocculent, and in general they are more soluble in hydrochloric acid than in water.

A solution of IODINE IN IODIDE OF POTASSIUM (containing 12.7 grm. free iodine in 1 litre) precipitates the solutions of the salts of all the alkaloids. The precipitates are brown and flocculent. Their formation and separation is assisted by acidifying with sulphuric acid. By washing the precipitate, dissolving it in solution of sulphurous acid and evaporating on the water-bath to remove the excess of sulphurous acid and the hydriodic acid, the alkaloid will remain in combination with sulphuric acid. If the precipitate was separated from a fluid containing a quantity of other organic substances, before proceeding as just stated, dissolve it in a dilute solution of hyposulphite of soda, filter, and re-precipitate with iodine solution.**

IODIDE OF MERCURY AND POTASSIUM precipitates the solutions of the salts of all the alkaloids. The precipitates are white or yellowish white, insoluble in water and dilute hydrochloric acid.

IODIDE OF CADMIUM AND POTASSIUM†† precipitates the solutions of salts of the alkaloids after acidification with sulphuric acid, even when very dilute. The precipitates are at first all flocculent and white, some of them soon become crystalline. They are insoluble in ether, readily soluble in alcohol, less soluble in water, readily soluble in excess of the precipitant. They have a tendency to decompose by long standing. The alkaloids may be obtained from the undecomposed precipitates by mixing with an alkaline carbonate or hydrate and water, and shaking with benzol, amylic alcohol, ether, or the like.

IODIDE OF BISMUTH AND POTASSIUM‡‡ added drop by drop to

* Zeitschr. f. anal. Chem. 6, 123. † *Ib.* 5, 406.
‡ Ann. d. Chem. u. Pharm. 104, 47. § *Ib.* 109, 179.
‖ Journ. f. prakt. Chem. 80, 211. ¶ Pharm. Centralhalle. 10r Jahrg., 131.

** By dissolving the brownish-red precipitate produced by mixing the iodine solution with a salt of strychnine in alcohol containing sulphuric acid and evaporating, prismatic crystals of strong polarizing power will be obtained (DE VRIJ and VAN DER BURG, Jahresber. von LIEBIG u. KOPP, 1857, 602). Until the optical properties of the analogous compounds of the other alkaloids shall have been examined we are unable to state whether this reaction is characteristic or not.

†† Prepared by saturating a boiling concentrated solution of iodide of potassium with iodide of cadmium, and adding an equal volume of cold saturated solution of iodide of potassium. The concentrated solution keeps well, but not the dilute.

‡‡ Prepared as follows:—Heat 32 parts of sulphide of bismuth in a combustion-tube sealed at one end with 41·5 parts of iodine, collect the iodide of bismuth in a receiver, purify it by resublimation, heat it with solution of iodide of potassium, filter hot, and add to the solution an equal volume of a cold saturated solution of iodide of potassium. The concentrated solution keeps well, but not the dilute. On mixing 10 c.c. water with 5 drops of concentrated sulphuric acid and adding 1 or 2 drops of the reagent, no turbidity should occur.

solutions of salts of the alkaloids acidified with sulphuric acid (10 c.c. of the alkaloid solution and five drops of concentrated sulphuric acid) produces almost immediately flocculent orange precipitates, in the case of nicotine, conine, morphine, narcotine, quinine, cinchonine, strychnine, brucine, atropine, and most other alkaloids; veratrine, on the other hand, gives only a faint turbidity. The precipitates formed with the first-named alkaloids agglutinate together to some extent when heated, they dissolve by long continued boiling, and separate again for the most part on cooling. None of the precipitates are crystalline. The alkaloids may be separated from the precipitates as given under the previous reagent.

PHOSPHOMOLYBDIC ACID* is precipitated by the solutions of all alkaloids, even when their quantity is very minute. The precipitates are light yellow, ochreous or brownish yellow, insoluble or difficultly soluble at the ordinary temperature in water, alcohol, ether, and dilute mineral acids, with the exception of phosphoric acid; they are most insoluble in dilute nitric acid, especially when it contains some of the reagent; acetic acid also is almost without action in the cold, but in the heat it has a solvent action. The precipitates dissolve in the hydrates and carbonates of the alkalies, generally with ease and with separation of the alkaloids. The latter may be removed by shaking with ether, amylic alcohol, benzol, or the like.

PHOSPHOANTIMONIC ACID, obtained by dropping perchloride of antimony into aqueous phosphoric acid, also precipitates ammonia and most of the alkaloids (not caffeine). The reactions are delicate, but they are generally less delicate than with the last reagent, especially in the case of nicotine and conine; this reagent is more delicate in one single instance, namely for atropine. The precipitates are usually flocculent and whitish, the brucine precipitate is rose-colored. On heating it dissolves, on cooling it separates again from the fluid which remains colored intensely carmine.

METATUNGSTIC ACID† precipitates the solutions of all the alkaloids. The precipitates are white and flocculent. The delicacy of the reactions is extreme. Acid solutions containing only one part of quinine or strychnine in 200,000, are rendered distinctly turbid, and deposit minute flocks in 24 hours.

PICRIC ACID precipitates almost all the alkaloids, even from solutions containing a large excess of sulphuric acid. The precipitates are yellow, and insoluble in excess of the precipitant; they are usually formed even in very dilute solutions. Morphine and atropine (pure) are only thrown down from neutral and concentrated solutions; the precipitates disappear on dilution (caffeine and pseudomorphine are not precipitated, likewise the glycosides).

* Prepared as follows:—Precipitate the nitric acid solution of molybdate of ammonia with phosphate of soda, wash the precipitate well, suspend it in water, and warm with addition of carbonate of soda, to complete solution. Evaporate to dryness, ignite the residue, and if reduction has taken place, moisten with nitric acid and ignite again. Warm with water, and dissolve by adding nitric acid in considerable excess. One part of the residue should make 10 parts of solution. The solution must be protected from ammoniacal fumes.

† Instead of the pure acid you may use a metatungstate acidified with mineral acid, or even ordinary tungstate of soda, with addition of phosphoric acid. Phosphoric acid, when added to an ordinary soluble tungstate, removes part of the base, and so produces a metatungstate.

## B. Properties and Reactions of the individual Alkaloids.

### I. Volatile Alkaloids.

The volatile alkaloids are fluid at the common temperature, and may be volatilized in the pure state as well as when mixed with water. They are accordingly obtained in the distillate when their salts are distilled with strong fixed bases and water. Their vapors, when brought in contact with those of volatile acids, form a white cloud.

### 1. Nicotina, or Nicotine ($C_{20}H_{14}N_2$).

§ 231.

1. Nicotina occurs in the leaves and seed of tobacco. In its pure state, it forms a colorless, oily liquid, of 1·048 sp. gr.; the action of air imparts a yellowish or brownish tint to it. It boils at 250°, suffering, however, partial decomposition in the process; but, when heated in a stream of hydrogen gas, it distils over unaltered, between 100° and 200°. It dissolves with ease in water, alcohol, and ether.

Nicotina has a peculiar, disagreeable, somewhat ethereal, tobacco-like odor. On heating it gives off a very powerful odor of tobacco. It has an acrid, pungent taste, and very poisonous properties. Dropped on paper, it makes a transparent stain, which slowly disappears; it turns turmeric-paper brown, and litmus-paper blue. Concentrated aqueous solution of nicotina shows these reactions more distinctly than the alkaloid in the pure state.

2. Nicotina has the character of a pretty strong base; it precipitates metallic oxides from their solutions, and forms salts with acids. The salts of nicotina are non-volatile, freely soluble in water and alcohol, insoluble in ether and amylic alcohol; they are inodorous, but taste strongly of tobacco; part of them are crystallizable. Their solutions, when distilled with solution of potassa, give a distillate containing nicotina. By neutralizing this with oxalic acid, and evaporating, oxalate of nicotina is produced, which may be freed from any admixture of oxalate of ammonia, by means of spirit of wine, in which the former salt is soluble, the latter insoluble.

3. If an aqueous solution of nicotina, or a solution of a salt of nicotina mixed with solution of soda or potassa, is shaken with *ether*, the nicotina is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass at 20° or 30°, the nicotina remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odor.

4. *Bichloride of platinum* produces in aqueous solutions of nicotina or its salts whitish-yellow flocculent precipitates. On heating the fluid containing the precipitate, the latter dissolves, but upon continued application of heat it very speedily separates again in form of an orange-yellow, crystalline, heavy powder, which, under the microscope, appears to be composed of roundish crystalline grains. If a rather dilute solution of nicotina, supersaturated with hydrochloric acid, is mixed with bichloride of platinum, the fluid at first remains clear; after some time, however, the double salt separates in small crystals (oblique, four-sided prisms), clearly discernible with the naked eye.

5. *Terchloride of gold* added in excess to aqueous solutions of the alkaloid or its salts produces a reddish-yellow flocculent precipitate, sparingly soluble in hydrochloric acid.

6. Solution of *iodine in iodide of potassium* and water, when added in small quantity to an aqueous solution of nicotina, produces a yellow precipitate, which after a time disappears. Upon further addition of iodine solution, a copious kermes-colored precipitate separates; but this also disappears again after a time. Solutions of the salts are precipitated with a kermes-brown color.

7. Solution of *tannic acid* produces in aqueous solution of nicotina, a copious white precipitate, which redissolves upon addition of hydrochloric acid.

8. If an aqueous solution of nicotina is added to excess of solution of *chloride of mercury*, an abundant, flocculent, white precipitate is formed. If solution of chloride of ammonium is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

## 2. Conia, or Conine ($C_{16}H_{15}N$).

### § 232.

1. Conia occurs in the leaves, seed, and flowers of the spotted hemlock. It forms a colorless oily liquid, of ·88 sp. gr.; the action of the air imparts to it a brown tint. In the pure state it boils at 168°; when heated in a stream of hydrogen gas, it distils over unaltered; but when distilled in vessels containing air, it turns brown and suffers partial decomposition; with aqueous vapors it distils over freely. It dissolves sparingly in water, 100 parts of water of the common temperature dissolving 1 part of conia. The solution turns turbid on warming, clear again on cooling. Conia is miscible in all proportions with alcohol and ether. The aqueous and alcoholic solutions manifest strong alkaline reaction. Conia has a very strong, pungent, repulsive odor, which affects the head, a most acrid and disagreeable taste, and very poisonous properties.

2. Conia is a strong base; it accordingly precipitates metallic oxides from their solutions, in a similar way to ammonia, and forms salts with acids. The salts of conia are soluble in water and in spirits of wine, ether also dissolves several of them (*e.g.* the sulphate) to some extent. Hydrochlorate of conia crystallizes readily; the smallest quantity of this base, brought in contact with a trace of hydrochloric acid, yields almost immediately a corresponding quantity of non-deliquescent rhombic crystals (Th. Wertheim). The sulphate does not crystallize except on very long standing.* The solutions of the salts turn brownish upon evaporation, with partial decomposition of the conia. The dry salts do not smell of the alkaloid; when moistened, they smell only feebly of it, but upon addition of solution of soda, they at once emit a strong odor. When salts of conia are distilled with solution of soda, the distillate contains conia. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with spirit of wine, the oxalate of conia is dissolved, whilst any oxalate of ammonia that may be present

* Zeitschr. f. anal. Chem. 1, 397.

is left undissolved. As conia is only sparingly soluble in water, and dissolves with still greater difficulty in solution of alkalies, a concentrated solution of a salt of conia turns milky upon addition of solution of soda. The minute drops which separate unite gradually, and collect on the surface.

3. If an aqueous solution of a salt of conia is shaken with *solution of soda* and *ether*, the conia is dissolved by the ether. If the latter is then allowed to evaporate on a watch-glass at 20° or 30°, the conia is left in yellowish-colored oily drops.

4. *Terchloride of gold* produces in solutions of the alkaloid or its salts a yellowish-white precipitate, insoluble in hydrochloric acid. *Chloride of mercury* gives with conia, a copious white precipitate, soluble in hydrochloric acid. *Bichloride of platinum* does not precipitate rather dilute aqueous solutions of salts of conia, the conia compound corresponding to ammonio-bichloride of platinum being insoluble in spirits of wine and ether, but tolerably soluble in water. The double salt also dissolves by boiling with alcohol; it separates in the amorphous form on cooling.

5. To solution of *iodine in iodide of potassium* and water, and to solution of *tannic acid*, conia comports itself like nicotina.

6. *Chlorine water* produces in a mixture of water and conia a strong, white turbidity.

The volatile alkaloids are most easily recognised when pure; the great object of the analyst must accordingly be to obtain them in that state. The way of effecting this is the same for nicotina as for conia, and has already been given in the foregoing paragraphs, viz., to distil with addition of solution of soda, neutralize with oxalic acid, evaporate, dissolve in alcohol, evaporate the solution, treat the residue with water, add solution of soda, shake the mixture with ether, and let the latter evaporate spontaneously. Conia is distinguished from nicotina chiefly by its odor, its sparing solubility in water, and its behavior with chlorine water.

## II. Non-volatile Alkaloids.

The non-volatile alkaloids are solid, and cannot be distilled over with water.

### FIRST GROUP.

### Non-volatile Alkaloids which are precipitated by Potassa or Soda from the Solutions of their Salts, and redissolve readily in an excess of the precipitant.

Of the alkaloids of which I purpose to treat here, one only belongs to this group, viz.,

### Morphia, or Morphine ($C_{34}H_{19}NO_6 = \overset{+}{M}o$).

### § 233.

1. Morphine occurs with the alkaloids codeine, thebaine, papaverine, narcotine, and narceine, and with meconic acid and meconine, in opium, the dried milky juice of the green capsules of the poppy (papaver som-

niferum). Crystallized morphia ($\dot{M}o + 2$ aq.) usually appears in the form of colorless, brilliant rhombic prisms, or, when obtained by precipitation, as a white crystalline powder. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol it requires about 90 parts by weight for solution; of boiling alcohol from 20 to 30 parts. The solutions of morphia in alcohol as well as in hot water manifest distinctly alkaline reaction. Morphine is nearly insoluble in ether, especially when crystallized, it dissolves in hot amylic alcohol, it is insoluble in benzole (RODGERS), and very difficultly soluble in chloroform (PETTENKOFER). Crystallized morphia loses both equivalents of water, at a moderate heat. Morphia may be sublimed unaltered by very cautious heating.*

2. Morphia neutralizes acids completely, and forms with them the SALTS OF MORPHIA. These salts are readily soluble in water and spirit of wine, insoluble in ether and amylic alcohol; their taste is disagreeably bitter. Most of them are crystallizable.

3. *Potassa* and *ammonia* precipitate from the solutions of salts of morphia—generally only after some time—$\dot{M}o + 2$ aq., in the form of a white crystalline powder. Stirring and friction on the sides of the vessel promote the separation of the precipitate, which redissolves with great readiness in an excess of potassa, but more sparingly in ammonia. It dissolves also in chloride of ammonium and, though with difficulty only, in carbonate of ammonia. On shaking a solution of morphia in potassa or soda with ether, very little of the alkaloid passes into the ether; on shaking with warm amylic alcohol, however, the whole of the alkaloid passes into the latter.

4. *Carbonate of potassa and carbonate of soda* produce the same precipitate as potassa and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphia in caustic potassa, or if carbonic acid is conducted into the solution, $\dot{M}o + 2$ aq. separates,—especially after ebullition—in the form of a crystalline powder. A more minute inspection, particularly through a lens, shows this powder to consist of small acicular crystals; magnified 100 times, these crystals present the form of rhombic prisms.

5. *Bicarbonate of soda and bicarbonate of potassa* speedily produce in solutions of neutral salts of morphia a precipitate of hydrated morphia, in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphia in the cold.

6. The action of strong *nitric acid* upon morphia or one of its salts, in the solid state or in concentrated solutions, produces a yellowish-red color. On addition of protochloride of tin no violet coloration occurs, as in the case of brucine. Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon heating they acquire a yellow tint.

* For the best way of subliming morphia, and for the value of the sublimate in microscopic diagnosis, see HELWIG (Zeitschr. f. anal. Chem. 3, 43; or Das Mikroscop in der Toxikologie von Dr. A. HELWIG. von Zabern. Mainz: 1864). In the latter work the subject is treated more completely and illustrated. I may mention that the alkaloid must be perfectly pure.

7. If morphia or a compound of morphia is treated with 4 or 5 drops of pure strong *sulphuric acid*, and warmed on a water-bath for 15 minutes, a colorless solution is obtained; if, after cooling, 10 to 20 drops of *sulphuric acid, mixed with nitric acid**, are added, and 2 or 3 drops of water, the fluid acquires a violet-red color (gentle heating promotes the reaction); and if now 4 or 5 clean lentil-sized fragments of *binoxide of manganese* are added, or a fragment of *chromate of potassium* (OTTO), the fluid acquires an intense mahogany color. If the fluid is then diluted with 4 parts of water, cooled in a test-tube, and ammonia added till the reaction is almost neutral, a dirty yellow color makes its appearance, which turns brownish red upon supersaturation with ammonia, without the deposition of any appreciable precipitate (J. ERDMANN). According to A. HUSEMANN† the violet coloration of sulphate of morphia by nitric acid, does not occur till the morphia solution has undergone change. It occurs immediately when the solution in strong sulphuric acid is heated to 100°—150°. If, after cooling, a drop of nitric acid is added, a splendid dark violet color is produced, which stays at the edge for several minutes, but in the middle soon passes into a blood-red color, which slowly becomes paler. Hypochlorite of soda acts like nitric acid. On heating morphia with sulphuric acid above 150°, a transient reddish violet color is produced, which turns finally to dirty green. If a solution which has thus been overheated is brought in contact after cooling with nitric acid, no bluish violet color is observed, but a reddish color is at once produced.

8. If a solution of *molybdic acid in concentrated sulphuric acid* (5 mgrm. molybdate of soda and 1 c.c. conc. sulphuric acid), is mixed with dry morphia or a dry salt of morphia, a magnificent reddish-violet color will make its appearance immediately; after a time the color will turn a dirty greenish brown. The experiment should be made in a small porcelain dish or watch-glass, and the mixture should be stirred with a glass rod. On further action of the air the fluid will become deep blue, commencing at the edge; this color will remain for hours (FRÖHDE).‡ If water is added to the blue fluid, this color vanishes, and a slightly turbid, dirty brown fluid is obtained; when this is filtered it yields a brown filtrate. (Difference from salicine.)

9. *Neutral sesquichloride of iron* imparts to *concentrated* neutral solutions of salts of morphia a beautiful dark blue color, which disappears upon the addition of an acid. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will appear less distinctly.

10. If *iodic acid* is added to a solution of morphia or of a salt of morphia, IODINE separates. In concentrated aqueous solutions the separated iodine appears as a kermes-brown precipitate, whilst to alcoholic and dilute aqueous solutions it imparts a brown or yellowish-brown color. The addition of starch-paste to the fluid, before or after that of the iodic acid, considerably heightens the delicacy of the reaction, since the blue tint of the iodide of starch remains perceptible in exceedingly dilute solutions, which is not the case with the brown color

* Mix 6 drops of nitric acid of 1·25 sp. gr. with 100 c.c. water, and add 10 drops of this mixture to 20 grammes of pure concentrated sulphuric acid.

† Zeitschr. f. anal. Chem. 3, 151. ‡ *Ibid.* 5, 214.

imparted by iodine. The reaction is most delicate when the iodic acid solution is mixed with starch-paste, and the dry morphia salt is added to the mixture. It need scarcely be mentioned that the delicacy of the reaction may also be increased by shaking with bisulphide of carbon. As other nitrogenous bodies (albumen, caseine, fibrine, &c.) likewise reduce iodic acid, this reaction has only a relative value; however, if *ammonia* is added after the iodic acid, the fluid becomes colorless if the separation of iodine has been caused by other substances, whilst the coloration becomes much more intense if it is owing to the presence of morphia (LEFORT).*

11. *Tannic acid* throws down in aqueous solutions of morphia salts, if they are not too dilute, white precipitates, readily soluble in acids.

### SECOND GROUP.

**NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS,** if the latter are not diluted in a larger proportion than 1 : 100; Narcotina, Quina, Cinchonia.

### a. NARCOTINA, or NARCOTINE ($C_{46}H_{25}NO_{14} = \dot{N}a$).

### § 234.

1. Narcotina accompanies morphia in opium (§ 233). Crystallized narcotina ($\dot{N}a$ + aq.) appears usually in the form of colorless, brilliant, straight rhombic prisms, or, when precipitated by alkalies, as a white, loose, crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but somewhat more readily upon heating. Chloroform dissolves it very easily, amylic alcohol with difficulty, benzole more readily. Solid narcotina is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotina does not alter vegetable colors. At 170° it fuses, with loss of 1 eq. of water.

2. Narcotina dissolves readily in acids, combining with them to salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation. Most of the salts of narcotine are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste.

3. *Pure alkalies*, and *alkaline carbonates* and *bicarbonates*, immediately precipitate from the solutions of salts of narcotine $\dot{N}a$ + aq. in the form

* LEFORT (Zeitschr. f. anal. Chem. 1, 134) recommends the following method for the detection of small quantities of morphia: moisten strips of very white unsized paper with the morphia solution, dry, and repeat the operation several times, so as to ensure absorption by the paper of a tolerably large quantity of the fluid; the dried paper contains the morphia in the solid state, most finely divided. Nitric acid, sesquichloride of iron, and iodic acid and ammonia will readily and with positive distinctness show the characteristic reactions on paper so prepared.

of a white powder, which, magnified 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitants. If solution of a salt of narcotina is mixed with ammonia, and ether added in sufficient quantity, the precipitate redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated on a watch-glass, the residue is seen, when magnified 100 times, to consist of small, distinct, elongated, and lance-shaped crystals.

4. *Concentrated nitric acid* dissolves narcotine to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. *Strong sulphuric acid* acts differently upon different specimens of narcotine. Those that are apparently the purest give a bluish violet solution which in a short time becomes dirty orange: specimens which appear less pure give a yellow solution at once. If the yellow solution in either case is warmed *very gradually* it becomes at first orange red, subsequently beautiful bluish violet, or purple blue stripes are seen proceeding from the edge, and finally, when the sulphuric acid begins to evaporate, an intense reddish violet color is formed. If the heating is interrupted when the blue color is present, the solution slowly becomes cherry red in the cold. The reaction is very delicate (HUSEMANN.)*

6. If to a solution of narcotine in strong sulphuric acid prepared in the cold, 10 to 20 drops of sulphuric acid containing a minute quantity of *nitric acid* (footnote, p. 350) are added, and then two or three drops of water, the fluid becomes intensely red. Slight warming is favorable to the reaction. Addition of binoxide of manganese does not change the color. If, after dilution, ammonia is added till the fluid is *nearly* neutral, the intensity of the color is diminished in consequence of the dilution. On addition of excess of ammonia a copious dark brown precipitate is finally produced (J. ERDMANN).

If to a solution of narcotine in strong sulphuric acid, prepared in the cold, chloride of soda is added, a distinct and rather permanent crimson color is produced, which passes into yellowish red. The solution of narcotine in strong sulphuric acid, which has been colored by heat, is turned immediately light yellow by nitric acid or chloride of soda, and a more reddish coloration appears gradually (HUSEMANN).

7. *Chlorine water* added to solution of a narcotine salt gives a yellow color, slightly inclining to green. On the addition of ammonia a yellowish red and much more intense color is produced.

8. If narcotine or a salt of narcotine is dissolved in excess of dilute *sulphuric acid*, mixed with finely powdered *binoxide of manganese*, and boiled for some minutes, the alkaloid is converted into opianic acid, cotarnine (a base soluble in water) and carbonic acid. On filtering, and adding ammonia to the filtrate, no precipitate will be obtained.

9. *Tannic acid* produces whitish precipitates in solutions of salts of narcotine. When the solutions are very dilute a mere turbidity is produced, but a precipitate is formed on addition of a drop of hydrochloric acid. The precipitate is very slightly soluble in hydrochloric acid.

* Zeitschr. f. anal. Chem. 3, 151.

### b. Quina, or Quinine ($C_{40}H_{24}N_2O_4 = \overset{+}{Q}$).

### § 235.

1. Quinine occurs in cinchona bark accompanying cinchonine. Crystallized quina, ($\overset{+}{Q} + 6$ aq.) appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in spirit of wine, both cold and hot, but less so in ether. The taste of quina is intensely bitter; the solutions of quina manifest alkaline reaction. Upon exposure to heat it loses the 6 eq. of water.

2. Quina neutralizes acids completely. The neutral salts taste intensely bitter; most of them are crystallizable, difficultly soluble in cold, readily soluble in hot water and in spirit of wine. The acid salts dissolve very freely in water; the solutions reflect a bluish tint. If a cone of light is thrown into them, by means of a lens either horizontally or vertically, a blue cone of light is seen even in highly dilute solutions.

3. *Potassa, ammonia,* and the neutral *carbonates of the alkalies* produce in solutions of salts of quina (if they are not too dilute) a white, loose, pulverulent precipitate of hydrated quina, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of an aggregate of crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of potassa, but more so in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. Chloride of ammonium increases its solubility in water. If a solution of quina is mixed with ammonia, ether added, and the mixture shaken, the quina redissolves in the ether, and the clear fluid presents two distinct layers. (In this point quina differs essentially from cinchonia, which by this means may be readily detected in presence of the former, and separated from it.)

4. *Bicarbonate of soda* also produces both in neutral and acid solutions of salts of quina a white precipitate. In acidified solutions containing 1 part of quina to 100 parts of acid and water, the precipitate forms immediately;—if the proportion of the quina to the acid and water is 1 : 150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is 1: 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more complete the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quina to a colorless fluid, turning yellowish upon application of heat.

6. The addition of *chlorine water* to the solution of a salt of quina fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green color. If, after the addition of the chlorine water, some solution of *ferrocyanide of potassium* is added, then a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction

is delicate and characteristic. Upon addition of an acid* to the red fluid, the color vanishes, but reappears afterwards upon cautious addition of ammonia. (O. LIVONIUS, communicated; A. VOGEL.)

7. *Concentrated sulphuric acid* dissolves pure quina and pure salts of quina to a colorless or very faint yellowish fluid; application of a gentle heat turns the fluid yellow, application of a stronger heat brown. Sulphuric acid containing an admixture of nitric acid dissolves quina to a colorless or very faint yellowish fluid.

8. *Tannic acid* produces a white precipitate in aqueous solutions of salts of quinine, even when they are exceedingly dilute. The precipitate is curdy and agglutinates on warming, it is soluble in acetic acid.

9. As regards HERAPATH'S quinine reaction, based upon the polarizing properties of sulphate of iodide of quinine, I refer to *Phil. Mag.* 6, 171.

### *c.* CINCHONIA, or CINCHONINE ($C_{40}H_{24}N_2O_2 = Ci$).

### § 236.

1. Cinchonine occurs in cinchona bark accompanying quinine. It appears either in the form of transparent, brilliant, rhombic prisms, or fine white needles, or, if precipitated from concentrated solutions, as a loose white powder. At first it is tasteless, but after some time a bitter taste of bark becomes perceptible. It is nearly insoluble in cold water, and dissolves only with extreme difficulty in hot water; it dissolves sparingly in cold dilute spirit of wine, more readily in hot spirit of wine, and the most freely in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonia separates upon cooling in a crystalline form. Solutions of cinchonia taste bitter, and manifest alkaline reaction. Cinchonia is insoluble in ether.†

2. Cinchonia neutralizes acids completely. The salts have the bitter taste of bark: most of them are crystallizable: they are generally more readily soluble in water and in spirit of wine than the corresponding quina compounds. Ether fails to dissolve them.

3. Cinchonia, when heated cautiously, fuses at first without loss of water; subsequently white fumes arise which, like benzoic acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long brilliant prisms are obtained (HLASIWETZ).

4. *Potassa*, *ammonia*, and the *neutral carbonates of the alkalies* produce in solutions of salts of cinchonia a white loose precipitate of CINCHONIA, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance even when magnified 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears under the microscope to consist of distinct crystalline needles aggregated into star-shaped tufts.

* Acetic acid answers the purpose best.

† The cinchonia of commerce usually contains in admixture another alkaloid, called cinchotina, which is soluble in ether. This alkaloid crystallizes in large rhomboidal crystals of brilliant lustre, which fuse at a high temperature, and cannot be sublimed, even in a stream of hydrogen gas (HLASIWETZ).

5. *Bicarbonate of soda* and *bicarbonate of potassa* precipitate cinchonia in the same form as in 4, both from neutral and acidified solutions of cinchonia salts, but not so completely as the monocarbonates of the alkalies. Even in solutions containing 1 part of cinchonia to 200 of water and acid, the precipitate forms immediately; its quantity, however, increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonia to a colorless fluid, which upon application of heat first acquires a brown, and finally a black color. Addition of some nitric acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, turns finally black.

7. The addition of *chlorine water* to the solution of a salt of cinchonia fails to impart a color to the fluid; if ammonia is now added, a yellowish-white precipitate is formed.

8. If the solution of a cinchonia salt containing only very little or no free acid, is mixed with ferrocyanide of potassium, a flocculent precipitate of ferrocyanide of cinchonia is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic (CH. DOLLFUS, BILL, SELIGSOHN).

9. *Tannic acid* produces a white flocculent precipitate in aqueous solutions of salts of cinchonia, the precipitate is soluble in a small quantity of hydrochloric acid, but is reprecipitated by addition of more hydrochloric acid.

*Recapitulation and Remarks.*

§ 237.

Narcotina and quina being soluble in ether, whilst cinchonia is insoluble, the two former alkaloids may be most readily separated by this means from the latter. For this purpose the analyst need simply mix the aqueous solution of the salts with ammonia in excess, then add ether, and separate the solution of quina and narcotine from the undissolved cinchonia. If the ethereal solution is now evaporated, the residue dissolved in hydrochloric acid and a sufficient amount of water to make the dilution 1 : 200, and bicarbonate of soda is then added, the narcotina precipitates, whilst the quina remains in solution. By evaporating the solution, and treating the residue with water, the quina is obtained in the free state.*

* The reaction with ammonia and ether fails to effect the separation of quinine from various other bases found associated with it, viz., $\alpha$ quinidine, $\beta$ quinidine, $\gamma$ quinidine, and cinchonidine; since, as G. KERNER (Zeitschr. f. anal. Chem. 1, 150) has shown, several of these other vegeto-alkalies are pretty freely soluble in ether. In fact, no qualitative reaction will enable the analyst to fully effect this purpose; but it may be accomplished by means of a simple volumetrical method, based upon the circumstance that the quina thrown down by ammonia from a solution of the sulphate, requires less ammonia to redissolve it than all the other vegeto-alkalies of the bark. Concerning the separation of quina from quinidine compare SCHWARZER (Zeitschr. f. anal. Chem. 4, 129), and concerning the separation of the cinchona alkaloids in general see VAN DER BURG (Zeitschr. f. anal. Chem. 4, 273).

THIRD GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT;* BUT ARE NOT PRECIPITATED FROM (even somewhat concentrated) ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnia, Brucia, Veratria, Atropia.

*a.* STRYCHNIA, or STRYCHNINE ($C_{42}H_{22}N_2O_4 = \overset{+}{S}r$).

§ 238.

1. Strychnia exists in company with brucine in various kinds of strychnos, especially in the fruit of strychnos nux vomica and of strychnos ignatius. It appears either in the form of white brilliant rhombic prisms, or, when produced by precipitation or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly insoluble in cold, and barely soluble in hot water. It is almost insoluble in absolute alcohol and ether, and only sparingly soluble in dilute spirit of wine. It dissolves freely in amylic alcohol, more especially with the aid of heat, likewise in benzole (RODGERS), and chloroform (PETTENKOFER). It does not fuse when heated. By cautious heating it may be sublimed unaltered (HELWIG), see foot-note § 233, 1.

2. Strychnia neutralizes acids completely. The salts of strychnia are, for the most part, crystallizable; they are soluble in water. All the salts of strychnia have an intolerably bitter taste, and are, like the pure alkaloid, exceedingly poisonous.

3. *Potassa* and *carbonate of soda* produce in solutions of salts of strychnia white precipitates of STRYCHNIA, which are insoluble in an excess of the precipitants. Magnified 100 times, the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnia separates only after the lapse of some time, in the form of crystalline needles, distinctly visible to the naked eye.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia; but after a short time—or if the solution is highly dilute, after a more considerable time—the strychnia crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Bicarbonate of soda* produces in neutral solutions of salts of strychnia a precipitate of strychnia, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline), the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to an acid solution of strychnia causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnia crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnia, supersaturated with bicarbonate of soda, is boiled for some time, a precipitate forms at once; from dilute solutions this precipitate separates only after concentration.

6. *Sulphocyanide of potassium* produces in concentrated solutions of

* Regarding atropine, see § 241, 4.

salts of strychnia immediately, in dilute solutions after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, truncated or pointed at an acute angle, and is but little soluble in an excess of the precipitant.

7. *Chloride of mercury* produces in solutions of salts of strychnia a white precipitate, which changes after some time to crystalline needles, aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution the double compound recrystallizes in larger needles.

8. If a few drops of pure *concentrated sulphuric acid* are added to a little strychnia in a porcelain dish, solution ensues, without coloration of the fluid. If small quantities of oxidizing agents (chromate of potassa, permanganate of potassa, ferricyanide of potassium, peroxide of lead, binoxide of manganese) are now added—best in the solid form, as dilution is prejudicial to the reaction—the fluid acquires a magnificent blue-violet color, which, after some time, changes to wine-red, then to reddish-yellow. With chromate of potassa and permanganate of potassa the reaction is immediate; on inclining the dish, blue violet streaks are seen to flow from the salt fragment, and by pushing the latter about, the coloration is soon imparted to the entire fluid. With ferricyanide of potassium the reaction is less rapid; but it is slowest with peroxides. The more speedy the manifestation of the reaction the more rapid is also the change of color from one tint to another. I prefer chromate of potassa, recommended by OTTO, or permanganate of potassa, recommended by GUY, to all other oxidizing agents. JORDAN succeeded, with chromate of potassa, in distinctly showing the presence of $\frac{1}{50000}$ grain of strychnia. J. ERDMANN prefers binoxide of manganese in lentil-sized fragments. Metallic chlorides and considerable quantities of nitrates, also large quantities of organic substances, prevent the manifestation of the reaction or impair its delicacy. It is therefore always advisable to free the strychnia first, as far as practicable, from all foreign matters before proceeding to try this reaction. If the solution colored red (by binoxide of manganese) is mixed with from 4 to 6 times its volume of water, heating being avoided, and ammonia is then added until the reaction is *nearly* neutral, the fluid shows a magnificent violet-purple tint; upon addition of more ammonia the color becomes yellowish-green to yellow (J. ERDMANN). I have found, however, that this reaction is seen only where larger, though still very minute, quantities of strychnia are present. Morphia interferes with this reaction.* In order to remove the morphine, the concentrated aqueous neutral solution of the substance is mixed with ferricyanide of potassium (NEUBAUER) or neutral chromate of potassa (HORSLEY) and filtered. The precipitate contains the strychnia, the solution the morphia. The precipitate is washed a little, dried, and mixed in a watch-glass with strong sulphuric acid. The blue-violet color is immediately produced. It should be borne in mind that the strychnia precipitates are not insoluble in water.† Finally I must mention that

* REESE, Zeitschr. f. anal. Chem. 1, 399. HORSLEY, *Ibid.* 1, 515. THOMAS, *Ibid.* 1, 517.

† RODGERS recommends to separate strychnia from morphia by benzole, in which the former alone is soluble. THOMAS recommends to render the solution of the acetates alkaline with potash, and to shake with chloroform; the morphia remains in the alkaline solution, while the strychnia dissolves in the chloroform.

curarine produces the same reaction with sulphuric acid and chromate of potassa as strychnia. They differ however in this, that curarine is colored red by sulphuric acid alone, and it gives much more permanent colorations with chromate of potassa than strychnine (DRAGENDORFF).

9. Strong *chlorine water* produces in solutions of strychnia salts a white precipitate, soluble in ammonia to a colorless fluid.

10. Strong *nitric acid* dissolves strychnia and its salts to a colorless fluid, which turns yellow when heated.

11. *Tannic acid* produces in solutions of strychnia salts heavy white precipitates, insoluble in hydrochloric acid.

### *b.* BRUCIA, or BRUCINE ($C_{46}H_{26}N_2O_8 = \overset{+}{Br}$).

### § 239.

1. Brucia occurs with strychnia (see § 238). Crystallized brucia ($\overset{+}{Br} + 8$ aq.) appears either in the form of transparent straight rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. Brucia is difficultly soluble in cold, but somewhat more readily in hot water. It dissolves freely in alcohol, both in absolute and dilute, also in cold, but more readily still in hot, amylic alcohol; but it is almost insoluble in ether. Its taste is intensely bitter. When heated, it fuses with loss of its water of crystallization. By cautious heating it may be sublimed unchanged (see foot-note § 233, 1).

2. Brucia neutralizes acids completely. The salts of brucia are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa* and *carbonate of soda* throw down from solutions of salts of brucia a white precipitate of brucia, insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, it appears to consist of very minute grains; but upon further inspection, these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves without exception into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces in solutions of salts of brucia a whitish precipitate, which appears at first like a number of minute drops of oil, but changes subsequently—with absorption of water—to small needles. The precipitate redissolves, immediately after separation, very readily in an excess of the precipitant; but after a very short time—or, in dilute solutions, after a more considerable lapse of time—the brucia, combined with crystallization water, crystallizes from the ammoniacal fluid in small concentrically grouped needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces in neutral solutions of salts of brucia a precipitate of brucia, combined with crystallization water; this precipitate separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare *Strychnia*). Bicarbonate of soda fails to precipitate acid solutions of salts of brucia; and it is only after the lapse of a considerable time, and with the escape

of the carbonic acid, that the alkaloid separates from the fluid in regular and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucia and its salts to intensely red fluids, which subsequently acquire a yellowish-red tint, and turn yellow upon application of heat. Upon addition of protochloride of tin or sulphide of ammonium to the heated fluid, no matter whether concentrated or after dilution with water, the faint yellow color changes to a most intense violet.

7. If a little brucia is treated with from 4 to 6 drops of pure *concentrated sulphuric acid*, a solution of a faint rose color is obtained, which afterwards turns yellow. If 10 or 20 drops of sulphuric acid mixed with some *nitric acid* (foot-note § 233, 7) are added, the fluid transiently acquires a red, afterwards a yellow color. Addition of binoxide of manganese transiently imparts a red, then a gamboge tint to the fluid. If the fluid is then, with proper cooling, diluted with 4 parts of water, and *ammonia* added to nearly neutral reaction, or even to alkaline reaction, the solution acquires a gold-yellow color (J. ERDMANN).

8. Addition of *chlorine water* to the solution of a salt of brucia imparts to the fluid a fine bright red tint; if ammonia is then added, the red color changes to yellowish-brown.

9. *Sulphocyanide of potassium* produces in concentrated solutions of salts of brucia immediately, in dilute solutions after some time, a granular crystalline precipitate, which, under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Chloride of mercury* also produces a white granular precipitate, which, under the microscope, appears composed of small roundish crystalline grains.

11. *Tannic acid* produces in solutions of salts of brucia, heavy dirty white precipitates, soluble in acetic acid, insoluble in hydrochloric acid.

### *c.* VERATRIA, or VERATRINE ($C_{64}H_{88}N_2O_{16}$) $\overset{+}{V}e$.

### § 240.

1. Veratria occurs in various species of veratrum, especially in the seeds of veratrum sabadilla (with veratric acid), and in the root of veratrum album (with jervine). It appears in the form of small prismatic crystals which acquire a porcelain-like look in the air, or as a white powder of acrid and burning, but not bitter taste; it is exceedingly poisonous. Veratria acts with great energy upon the membranes of the nose; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water; in alcohol it dissolves readily, but more sparingly in ether. At 115° it fuses like wax, and solidifies upon cooling to a transparent yellow mass. By cautious heating it may be sublimed unchanged (see foot-note § 233, 1).

2. Veratria neutralizes acids completely. Some salts of veratria are crystallizable, others dry up to a gummy mass. They are soluble in water, and have an acrid and burning taste.

3. *Potassa, ammonia,* and the *monocarbonates of the alkalies* produce in solutions of salts of veratria a flocculent white precipitate, which, viewed under the microscope immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its

appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa or of carbonate of potassa. It is slightly soluble in ammonia in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda* and *bicarbonate of potassa* the salts of veratria comport themselves like those of strychnia and brucia. However, the veratria separates readily upon boiling, even from dilute solutions.

5. If veratria is acted upon by *concentrated nitric acid*, it agglutinates into small resinous lumps, which afterwards dissolve slowly in the acid. If the veratria is pure the solution is colorless.

6. If veratria is treated with *concentrated sulphuric acid*, it also agglutinates at first into small resinous lumps; but these dissolve with great readiness to a faint yellow fluid, the color of which gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red, and finally to purple red. The color persists 2 or 3 hours, then disappears gradually. Addition of sulphuric acid, containing nitric acid, or of binoxide of manganese causes no great change of color. If the fluid is then diluted with water, and ammonia added until the reaction is nearly neutral, a yellowish solution is obtained, in which ammonia added in excess produces a greenish light-brown precipitate (J. ERDMANN).

7. If veratria is dissolved in *strong hydrochloric acid*, a colorless fluid is obtained, which by long boiling acquires an intensely red tint, permanent on standing. The reaction is very delicate, and occurs not only with the perfectly pure veratrine but with the ordinary commercial alkaloid (TRAPP).

8. *Sulphocyanide of potassium* produces only in concentrated solutions of salts of veratria flocculent, gelatinous precipitates.

9. Addition of *chlorine water* to the solution of a salt of veratria imparts to the fluid a yellowish tint, which upon addition of ammonia, changes to a faint brownish color. In concentrated solutions chlorine produces a white precipitate.

### *d.* ATROPIA, or ATROPINE ($C_{34}H_{23}NO_6$).

### § 241.

1. Atropia occurs in all parts of the deadly nightshade (atropa belladonna), and of the thorn-apple (datura stramonium). It forms small brilliant prisms and needles. It is, when pure, without odor and nauseously bitter; it fuses at 90°, and volatilizes at 140° with partial decomposition. By heating between watch-glasses it volatilizes without blackening. The sublimate is soft and oily. Atropia dissolves in about 300 parts of cold water, and 60 parts of boiling water, it is very soluble in alcohol, the saturated alcoholic solution is precipitated by the addition of a small quantity of water. It is very soluble in chloroform and amylic alcohol, but it requires about forty parts of ether for solution.

2. Atropia combines with acids, forming salts, some of which, particularly the acid salts, do not crystallize. The salts dissolve easily in water and alcohol, scarcely at all in ether. The aqueous solutions of the salts acquire a dark color by long heating.

3. Atropia and its salts are active narcotic poisons. When applied to the eye they dilate the pupil for a considerable time. Hyoscyamine has the same action; but the dilatation in this case is rather slower in making its appearance and more lasting.

4. *Potassa* and *monocarbonates of the fixed alkalies* added to concentrated aqueous solutions of salts of atropia precipitate a portion of the alkaloid. The precipitate, which is at first pulverulent, does not dissolve in excess of the precipitant more readily than in water. By long standing it becomes crystalline. *Ammonia* likewise produces a precipitate, soluble in excess. Atropia is decomposed, in contact with fixed alkalies or with baryta water, slowly in the cold, rapidly on heating.

5. *Carbonate of ammonia* and *bicarbonates of the alkalies* do not precipitate solutions of salts of atropia.

6. *Terchloride of gold* added to aqueous solutions of salts of atropia throws down a compound of hydrochlorate of atropia and terchloride of gold in the form of a yellow precipitate which gradually turns crystalline.

7. *Tannic acid* produces in aqueous solutions of salts of atropia a white curdy precipitate soluble in ammonia.

8. If atropia is warmed with concentrated *sulphuric acid* to slight browning, and a few drops of water are added to the watch-glass, an agreeable odor is evolved, recalling the sloe blossom, or perhaps more the cheese rennet (galium verum). On further heating the odor increases.

9. *Cyanogen gas* passed into a sufficiently concentrated alcoholic solution of atropia produces a reddish-brown color (HINTERBERGER).

10. *Picric acid* does not precipitate solutions of pure salts of atropia. Consequently solutions of atropia which after acidification with dilute sulphuric acid give a precipitate with this reagent, must be considered to contain some other unknown alkaloid (HAGER).

### *Recapitulation and Remarks.*

### § 242.

Strychnia may be separated from brucia, veratria, and atropia by means of absolute alcohol, since it is insoluble in that menstruum, whilst the latter alkaloids readily dissolve in it. The identity of strychnia is best established by the reaction with sulphuric acid and the above-mentioned oxidizing agents;* also by the form of its crystals—when thrown down by alkalies—viewed under the microscope; and lastly, by the form of the precipitates produced by sulphocyanide of potassium and chloride of mercury. Brucia and veratria may be separated from atropia by shaking the alkaline solution with petroleum ether (DRAGENDORFF). The latter takes up the brucia and veratria, but not the atropia. By separating the aqueous fluid from the petroleum ether and shaking it with ether the atropia may be obtained in ethereal solution. Brucia and veratria are not readily separated from one another, but may

* The only substance which besides curarine (see above), shows somewhat analogous reactions in this respect, is aniline. A. GUY has, however, called attention to the fact that aniline, treated with sulphuric acid and oxidizing agents, acquires a pale green color at first, which gradually deepens, and only then changes to a magnificent blue, which, after persisting some time, turns finally black.

be detected in presence of each other. The identity of brucia is best established by the reactions with nitric acid and protochloride of tin or sulphide of ammonium, or by the form of the crystalline precipitate which ammonia produces in solutions of salts of brucia. Veratria is sufficiently distinguished from brucia and the other alkaloids which we have treated of, by its characteristic deportment at a gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratria in presence of brucia, the reaction with concentrated sulphuric acid or with hydrochloric acid is selected.

## C. Properties and Reactions of certain non-nitrogenous Bodies, allied to the Alkaloids, viz., Salicine, Digitaline, and Picrotoxine.

### § 243.

### *a.* Salicine ($C_{26}H_{18}O_{14}$).

1. Salicine exists in the bark and leaves of most kinds of willow and some kinds of poplar. It appears either in the form of white crystalline needles and scales of silky lustre, or, where the crystals are very small, as a powder of silky lustre. It has a bitter taste, is readily soluble in water and alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. If salicine is treated with *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving; the color of the sulphuric acid is at first unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid* and boiled for a short time, it suddenly becomes turbid with formation of sugar and deposits a white agglutinating precipitate (saliretine). If the precipitated liquor is now mixed with 1 or 2 drops of chromate of potassa and boiled, the saliretine will acquire a bright rose color, the characteristic odor of salicyligenic acid being emitted at the same time.

### § 244.

### *b.* Digitaline ($C_{56}H_{40}O_{20}$?)

1. Digitaline exists in the leaves, seeds, and capsules of the foxglove (digitalis purpurea). It is usually white, amorphous, but it may also be obtained in crystals.* It is without odor, bitter, and an active poison, its powder irritates the eyes and causes sneezing. At 180° it becomes colored but does not fuse, above 200° it is completely decomposed.

2. Digitaline is neutral. It dissolves in all proportions in chloroform, and in about 12 parts of alcohol of 90° at the ordinary temperature, but more readily on boiling; it is less soluble in absolute alcohol. It is only very slightly soluble in ether free from alcohol. It is very difficultly soluble in water, even when boiling (1 part requires 1000 parts of boiling water), the solution, however, has a very bitter taste.

* Nativelle gives a method for preparing crystallized digitaline, see Journ. de Pharm. 9, 255—Zeitschr. f. Chem. 5, 401—Chem. Centr. Bl. 1870, 30. The commercial digitaline is frequently a mixture of various bodies, and this explains why the properties of digitaline as given by different chemists are found to vary so greatly.

3. When digitaline is dissolved in *concentrated sulphuric acid* (to which it imparts a green color), and the solution is stirred with a rod dipped in *bromine water*, a violet reddish coloration makes its appearance (GRANDEAU, J. OTTO). When the experiment is made in the manner directed the reaction is very delicate and characteristic. Delphinine only shows a similar deportment; but when an acid solution is shaken with ether delphinine does not pass into the ether, while digitaline does (OTTO).

4. *Hydrochloric acid* dissolves digitaline with a greenish yellow color; water precipitates a resinous body from this solution. *Nitric acid* dissolves it with evolution of red fumes. *Acetic acid* dissolves it without being colored.

5. On shaking a solution of digitaline, even if acid, with *ether*, the digitaline passes into the ether (J. OTTO).

6. The solutions of digitaline are not precipitated by *solution of iodine*, *picric acid*, and *metallic salts*, but they are precipitated by *tannic acid*. The precipitate is somewhat soluble in boiling water.

7. On boiling digitaline with *dilute sulphuric acid* sugar and digitaliretine are formed (WALZ, KOSSMANN). The former may be recognised by its power of reducing alkaline solution of copper, the latter crystallizes from hot alcohol in brilliant grains (KOSSMANN). J. OTTO says that on boiling down a solution of digitaline in dilute sulphuric acid an odor recalling infusion of digitalis is noticed.

## § 245.

### *c.* PICROTOXINE ($C_{30}H_{12}O_8$).

1. Picrotoxine is the poisonous principle of the fruit of menispermum cocculus. It forms white brilliant four-sided prisms or needles. It is without odor, very bitter, a narcotic poison, fuses when heated, yielding empyreumatic fumes.

2. Picrotoxine is neutral. It dissolves in water, especially when hot, with tolerable ease, and crystallizes from the solution in needles on cooling and evaporation. Hot alcohol dissolves it with extreme facility. The concentrated solution solidifies when cold to a silky mass, more dilute solutions give silky needles when evaporated. Picrotoxine is difficultly soluble in ether. The latter does not withdraw it from aqueous or alkaline solution, but it does withdraw it from acidified solutions (G. GÜNKEL). The ethereal solution when evaporated leaves the picrotoxine in the form of powder or scaly crystals.

3. *Acids* do not neutralize picrotoxine, and, with the exception of acetic acid, do not increase its solubility in water.

4. *Ammonia*, *potassa*, and *soda* dissolve picrotoxine freely. Acids, even carbonic acid, precipitate it from the concentrated solutions. Picrotoxine therefore possesses the character of an acid rather than of a base. The solutions of picrotoxine in potassa or soda when heated acquire a yellow or yellowish red color.

5. If a solution of picrotoxine containing potassa or soda is mixed with a solution of *tartrate of copper and potassa* and warmed gently, suboxide of copper separates.

6. *Solution of iodine*, *picric acid*, *tannic acid*, *and metallic salts* do not precipitate solutions of picrotoxine.

## Systematic Course for the Detection of the Alkaloids and of Salicine, Digitaline, and Picrotoxine.

In the methods described under I. and II., it is presupposed that the *non-volatile* alkaloids, &c., are in concentrated solution, dissolved in water by the agency of acids, and free from any substances which would obscure or modify the reactions. Under III. will be described methods to be used in the presence of coloring or extractive matters, and for the detection of *volatile* alkaloids.

### I. Detection of the non-volatile Alkaloids, &c., in Solutions containing only one of these Substances.*

### § 246.

1. To a portion of the solution add a drop of dilute sulphuric acid and then some solution of iodine in iodide of potassium or of phosphomolybdic acid.

*a. No precipitate is formed.* Absence of all alkaloids, possible presence of salicine, digitaline, picrotoxine. Pass on to 5.

* Where the detection of one of the five more frequently occurring poisonous alkaloids alone is the object, the following simple method, devised by J. Erdmann, will fully answer the purpose.

In this method, which is more especially applicable in cases where the disposable quantity of substance is very small, the alkaloids are supposed to be present in the pure state and in the solid form.

1. Treat the substance with 4 or 6 drops of pure concentrated sulphuric acid.

Yellow color, speedily changing to red: Veratria.

Rose color, changing afterwards to yellow: Brucia.

The other alkaloids, if pure, impart no color to the sulphuric acid. (See Husemann's statement in opposition, § 234, 5.)

2. No matter whether there is color or not, add to the fluid obtained in 1, 10 or 20 drops of concentrated sulphuric acid mixed with nitric acid (see foot-note to § 233, 7), then 2 or 3 drops of water. After a quarter or half-hour the fluid shows:

*a.* a violet-red color: Morphia;

*b.* an onion-red color: Narcotina;

*c.* a transient-red tint, changing to yellow: Brucia;

*d.* the red color of the sulphuric acid solution of Veratria is not materially altered;

*e.* with strychnia no coloration is observed.

3. Put into the fluid obtained in 2, no matter whether colored or not, 4 or 6 clean fragments of binoxide of manganese, of the size of a lentil. After an hour the fluid shows:

*a.* a mahogany-brown color: Morphia;

*b.* a yellowish-red to blood-red color: Narcotina;

*c.* a transient purple-violet tint, changing to deep onion-red: Strychnia;

*d.* a transient red tint, changing to gamboge-yellow: Brucia;

*e.* a dark dirty cherry-red color: Veratria.

4. Pour the colored fluid obtained in 3, into a test tube containing 4 times the volume of water, and add ammonia until the neutralization point is *almost* attained. Heat must be as much as possible avoided in these operations.

*a.* dirty-yellow color, changing to brownish-red upon supersaturation with ammonia, without immediate deposition of a notable precipitate: Morphia;

*b.* reddish coloration, more or less intense according to the degree of dilution; upon supersaturation with ammonia, copious dark-brown precipitate: Narcotina.

*c.* violet-purple colored solution, becoming yellowish-green to yellow upon addition of ammonia in excess: Strychnia.

*d.* gold-yellow solution, not materially changed by excess of ammonia: Brucia;

*e.* faint brownish solution, turning yellowish upon further addition of ammonia, and depositing a greenish light-brown precipitate: Veratria.

*b. A precipitate is formed.* There is cause to suspect the presence of an alkaloid; pass on to 2.

2. To a portion of the aqueous solution add dilute potassa or soda drop by drop, till the fluid acquires a scarcely perceptible alkaline reaction, stir, and allow to stand for some time.

*a. No precipitate is formed:* this is a positive indication, if the solution was concentrated, of the absence of all alkaloids; but if the solution was dilute, there is a possibility that ATROPIA may be present. Test further portions of the solution therefore if necessary according to § 241 with terchloride of gold, tannic acid, and heating with sulphuric acid.

*b. A precipitate is formed.* Add potassa or soda drop by drop till the fluid is strongly alkaline, and if it does not become clear, water also.

*a. The precipitate disappears:* morphia or atropia. Test a fresh portion of the solution with iodic acid (§ 233, 10).

*aa. Separation of iodine:* MORPHIA. Confirm by § 233, 7 & 8.

*bb. No separation of iodine:* ATROPIA. Confirm as in *a.*

*β. The precipitate does not disappear:* presence of an alkaloid of the second or third group (atropia excepted). Pass on to 3.

3. To another portion of the original solution add two or three drops of dilute sulphuric acid, then a saturated solution of bicarbonate of soda, till the acid reaction just vanishes; stir actively with a glass rod, rubbing the sides of the vessel and allow to stand half an hour.

*a. No precipitate is formed:* absence of narcotina and cinchonia. Pass on to 4.

*b. A precipitate is formed:* narcotina, cinchonia, perhaps also quina (since its precipitation by bicarbonate of soda is entirely dependent on the amount of water present). To a portion of the original solution add ammonia in excess, then a sufficient quantity of ether, and shake.

*a. The precipitate redissolves in the ether, the clear fluid presenting two distinct layers.* Narcotina or quina. To distinguish between them test a fresh portion of the original solution with chlorine water and ammonia. If the solution turns green, QUINA is present, if yellowish-red, NARCOTINA is present. To confirm for narcotina apply the test with sulphuric acid containing nitric acid (§ 234, 6).

*β. The precipitate does not redissolve in the ether:* CINCHONIA. To confirm try the deportment on heating (§ 236, 3) or to ferrocyanide of potassium (§ 236, 8).

4. Put a portion of the original substance or of the residue obtained by evaporating the original solution, in a watch-glass, and add concentrated sulphuric acid.

*a.* A rose-colored solution is obtained, which becomes intensely red upon addition of nitric acid: BRUCIA. Confirm by nitric acid and protochloride of tin (§ 239, 6).

*b.* A yellow solution is obtained, which gradually turns yellowish-red, blood-red, and crimson: VERATRIA.

*c.* A colorless solution is obtained, which remains colorless on standing. Add a fragment of chromate of potassa, a deep blue

coloration indicates STRYCHNIA, no change indicates QUINA. Confirm by chlorine water and ammonia.

5. To determine whether salicine, digitaline, or picrotoxine are present, mix a fresh portion of the original solution with tannic acid.

*a. A dirty white flocculent precipitate:* DIGITALINE may be suspected. Test for it with sulphuric acid and bromine water (§ 244, 3).

*b. No precipitate is formed.* Make a portion of the original solution barely alkaline with soda solution, add a solution of tartrate of copper and potassa, and warm.

*α. Suboxide of copper is thrown down:* PICROTOXINE may be suspected. Acidify a portion of the original solution, add ether, shake, pour off the ethereal layer, and let it evaporate. If picrotoxine is present, it will remain, and may be further tested by § 245.

*β. No suboxide of copper is thrown down:* SALICINE may be suspected. Test for it by boiling with dilute hydrochloric acid, &c., according to § 243, 4, and by concentrated sulphuric acid, according to § 243, 3.

## II. DETECTION OF THE NON-VOLATILE ALKALOIDS, &c., IN SOLUTIONS WHICH MAY CONTAIN ALL THESE SUBSTANCES.

### § 247.

1. Acidify the solution with hydrochloric acid, add pure ether free from alcohol, shake, pour off the ether, and allow it to evaporate in a glass dish.

*a. No residue remains:* absence of digitaline and picrotoxine. Pass on to 2.

*b. A residue remains:* digitaline and picrotoxine may be suspected (it must not be forgotten that other substances might pass into ethereal solution under these circumstances, such as oxalic acid, tartaric acid, lactic acid, OTTO). Add fresh ether to the aqueous residue, shake again and pour off, in order to remove whatever is soluble in ether as completely as possible, and let the ether evaporate. Proceed with the aqueous residue according to 2, and treat the residue of the ether solution, which may contain traces of atropia, as follows:—

*α.* Dissolve a portion in alcohol, and allow the solution to evaporate slowly: long silky needles radiating from a point indicate PICROTOXINE. Confirm according to § 245.

*β.* Dissolve a portion in concentrated sulphuric acid, and add bromine water. A reddish color indicates DIGITALINE. Confirm by § 244.

*γ.* Traces of ATROPIA can only be recognised by the property of the aqueous solution of the residue to dilate the pupil.

2. To a portion of the aqueous solution add a solution of iodine in iodide of potassium, to another portion add some phosphomolybdic acid.

*a. A precipitate is produced in both cases:* alkaloids are indicated. Pass on to 3.

*b. No precipitate is produced in either case:* alkaloids are contra-indicated. Pass on to test for salicine according to § 243.

3. To a small portion of the aqueous solution add potassa or soda till just alkaline, observe whether or no a precipitate is produced, then add potassa or soda in good excess and dilute.

*a. No precipitate was produced by potassa or soda, or a precipitate so produced has redissolved:* presence of atropia or morphia, absence of all other alkaloids. Mix a fresh and larger portion of the aqueous solution with bicarbonate of potassa or soda in excess, stir, and allow to stand some time.

*α. No precipitate is produced:* absence of morphia. Shake the fluid with ether, separate the ether, allow it to evaporate, and test the residue for ATROPIA by § 241, 6, 7, 8.

*β. A precipitate is produced:* MORPHIA. Filter, treat the filtrate according to *a*, to test for atropia, and test the precipitate for morphia according to § 233, 7 and 8.

*b. A precipitate was produced by potassa or soda, which would not redissolve in excess of the precipitant or by moderate dilution:* treat a larger portion of the acidified aqueous fluid like the small portion above, and filter. Proceed with the precipitate according to 4. Shake the alkaline filtrate with ether, allow to stand for an hour (so that the morphia which has at first dissolved in the ether may separate again as completely as possible), and separate the ether. Allow the ether to evaporate, and test the residue for ATROPIA according to § 241, 6, 7, 8. Separate the MORPHIA from the aqueous layer by carbonic acid (§ 233, 4) and test it according to § 233, 7 and 8.

4. Wash the precipitate filtered off in 3, *b*, with cold water, dissolve it in slight excess of dilute sulphuric acid, add solution of bicarbonate of soda till the fluid is neutral, stir actively, rubbing the sides of the vessel, and allow to stand for an hour.

*a. No precipitate is formed:* absence of narcotina and cinchonia. Boil the solution nearly to dryness, and take up the residue with cold water. If nothing insoluble remains, pass on to 6; if a residue does remain, examine it by 5 for quina (of which a small amount may be present) strychnia, brucia, and veratria.

*b. A precipitate is formed.* (This may contain narcotina, cinchonia, and quina, compare § 246, 3, *b*). Filter, proceeding with the filtrate according to *a*, with the precipitate as follows:—Wash it with cold water, dissolve in a little hydrochloric acid, add ammonia in excess, and then a sufficient quantity of ether.

*a. The precipitate has completely dissolved in the ether, and two clear layers of fluid are formed:* absence of cinchonia, presence of quina or narcotina. Evaporate the ethereal solution, take up the residue with a little hydrochloric acid, add water till the dilution is at least 1 : 200, then bicarbonate of soda till neutral, and allow to stand for some time. A precipitate indicates NARCOTINA: confirm by chlorine water and ammonia, also by sulphuric acid containing nitric acid (§ 234). Evaporate the clear fluid or the filtrate from the narcotina to dryness, and treat with water. If a residue remains, wash it, dissolve in

hydrochloric acid, and add chlorine water and ammonia; a green coloration indicates QUINA.

*β. The precipitate has not dissolved in the ether, or not completely:* CINCHONIA, perhaps also quina or narcotina. Filter, and test the filtrate as in *a* for quina and narcotina; the precipitate consists of cinchonia, and may be further tested according to § 236, 3 or 8.

5. Wash the insoluble residue of 4, *a*, with water, dry it in a water-bath, and digest with absolute alcohol.

*a. It dissolves completely:* absence of strychnia, presence of (quina) brucia or veratria. Evaporate the alcoholic solution on the water-bath to dryness, and, if quina has already been detected, divide the residue into two portions, and test one part for BRUCIA, with nitric acid and protochloride of tin (§ 239, 6), the other for VERATRIA, by means of concentrated sulphuric acid (§ 240, 6); but if no quina has as yet been detected, divide the residue into three portions, *a*, *b*, *c*; examine *a* and *b* for BRUCIA and VERATRIA, in the manner just stated, and *c* for QUINA, with chlorine water and ammonia. However, if brucia is present, dissolve *c* in hydrochloric acid, add ammonia and ether, let the mixture stand for some time, evaporate the ethereal solution, and examine the residue for quina.

*b. It does not dissolve, or at least not completely:* presence of STRYCHNIA, perhaps also of (quina) brucia and veratria. Filter, and examine the filtrate for (QUINA) BRUCIA and VERATRIA as directed in *a*. The identity of the precipitate with strychnia is demonstrated by the reaction with sulphuric acid and chromate of potassa (§ 238, 8).

6. To the rest of the acidified solution which has been exhausted with ether, add more hydrochloric acid and boil for some time. If a precipitate is formed, the presence of SALICINE is indicated. Confirm by adding chromate of potassa to the precipitated fluid and boiling (§ 243, 4) and by testing the original substance with concentrated sulphuric acid (§ 243, 3).

### III. Detection of the Alkaloids and of Digitaline and Picrotoxine in Presence of Extractive and Coloring Vegetable or Animal Matters.

The presence of mucilaginous, extractive, and coloring matters renders the detection of the alkaloids a task of considerable difficulty. These matters obscure the reactions so much that we are even unable to determine by a preliminary experiment, whether the substance under examination contains alkaloids or not. I will now give several methods by means of which the separation of the alkaloids from such extraneous matters may be effected, and their detection made practicable. Which of these methods to select will depend upon the particular circumstances of the case.

### 1. Method of *Stas** for the Detection of Poisonous Alkaloids (and of Digitaline and Picrotoxine), modified by *J. Otto*.†

§ 248.

Stas's process depends upon the following facts:

*a.* The acid salts of the alkaloids are soluble in water and alcohol.

*β.* The neutral and acid salts of the alkaloids are generally insoluble in ether. Hence salts of the alkaloids do not usually pass into ethereal solution when the neutral or acid solution is shaken with ether, and hence also the alkaloids pass into aqueous solution as acid sulphates when the ethereal solution of the pure alkaloid is shaken with dilute sulphuric acid.

*γ.* If aqueous solutions containing the neutral or acid salts of alkaloids are mixed with caustic, carbonated or bicarbonated alkalies, the alkaloids are liberated, and if now ether or amylic alcohol is added and the mixture is shaken, the pure alkaloids pass into solution in the latter fluid.

It will be evident from the following that there are certain exceptions to these general rules.

*a.* If you have to look for alkaloids in the contents of a stomach or intestines, in food, or generally in pappy matters, mix the substance with twice its weight of strong pure alcohol, and just enough tartaric acid to give a decided reaction, and warm to 70° or 75°. Allow to cool thoroughly, filter, and wash with strong pure alcohol.

If you have to deal with the heart, liver, lungs, or similar organs, cut them into fine shreds, moisten with the acidified alcohol, squeeze, repeat the operation till the substance is exhausted, and filter the mixed fluids.

*b.* Evaporate the alcoholic fluids at a rather low temperature. This may be done on a water-bath, keeping the water at about 80°. The solution under these circumstances will not rise higher than 40 or 50°. If this temperature is considered too high, you may hasten the evaporation by blowing air across the surface of the solution. Stas considers that the temperature should not exceed 35°; he therefore evaporates under a bell-glass over sulphuric acid, with or without the aid of an air pump, or in a retort with a current of air passing through it. Such extreme caution, however, is very rarely necessary; at all events, the principal bulk of the fluid may always be evaporated off on a gently heated water-bath.

If insoluble substances separate on evaporation (fat, &c.), as indeed is usually the case, filter the now aqueous fluid through a moistened filter, and evaporate the filtrate and washings as above described to the consistence of an extract. If no insoluble substances separate on evaporating the alcoholic fluid, you may, of course, at once evaporate to the consistence of an extract.

* Bull. de l'Académie de Médecine de la Belgique, 9, 304—Jahrb. f. prakt. Pharm. 24, 313—Jahresb. von Liebig u. Kopp, 1851, 640.

† Annal. der Chem. u. Pharm. 100, 44—Otto's Anleit. zur Ausmittel. der Gifte, 3 ed., 33.

*c.* To the residue left on evaporation, add gradually small portions of cold absolute alcohol, mix intimately, and finally add a large quantity of alcohol, in order to separate everything that can be precipitated by it. Filter the alcoholic extract through a filter moistened with alcohol, wash the residue with cold alcohol, evaporate the alcoholic solution at a low temperature (see above), take up the residue with a little water, neutralize the greater part of the free acid with dilute soda, leaving the solution distinctly acid, and shake with pure ether, free from alcohol and oil of wine (OTTO). By the aid of a separating funnel, or an ordinary burette, separate the ether from the aqueous layer, and wash the latter again and again with fresh ether, until the ether is no longer colored. The ether takes up besides coloring matters also picrotoxine and digitaline (and colchicine). It is advisable to keep the first strongly colored ethereal extract apart from the subsequent ethereal washings, so that they may be examined separately (compare *h*).

*d.* Warm the aqueous solution which has been separated from ether gently, to remove the dissolved ether, and add solution of soda cautiously, till the fluid gives a distinct reaction with turmeric paper. The alkaloids are thus liberated, morphia dissolving in the excess of soda. Shake the fluid with pure ether, and after half an hour or an hour, separate the two layers of fluid as in *c*. The ethereal extract contains the whole of the alkaloids, except morphia, only a small part of which dissolves in it. The amount of morphia dissolved by the ether is the smaller, the more completely the acidified aqueous solution was freed from dissolved ether, and the longer the time which was allowed to elapse between the shaking with ether and the separation of the two layers of fluid. Allow a portion of the ethereal extract to evaporate in a large watch-glass, which should be heated to about 25° or 30° (to prevent condensation of water). If no residue remains, no alkaloid was dissolved in the ether; pass on to *g*. If a residue does remain, its appearance will give you some idea of the nature of the alkaloid: thus oily streaks which gradually collect to a drop, and when gently warmed give an unpleasant suffocating odor, would indicate a fluid, volatile base; while again a solid residue, or a turbid fluid containing solid particles in suspension, would indicate a non-volatile solid base. If the ethereal extract has left a residue, repeat the treatment of the aqueous fluid with fresh supplies of ether, till a portion of the last ethereal washings leaves no residue on evaporation. Allow the mixed ethereal extracts to evaporate in a small glass dish placed upon a bath containing water at about 30°, keeping the little dish filled up by the addition of fresh quantities.

The aqueous fluid which contains the morphia is to be examined according to *g*.

*e.* If the acidified aqueous fluid in *c* has been well exhausted with ether, on the evaporation of the ethereal extract the alkaloids will remain in so pure a state, that the tests may be applied at once to the residue. If the residue consists of oily streaks or drops, complete the evaporation in a vacuum over sulphuric acid, in order to remove the remainder of the ether and ammonia, and then test for conia and nicotina according to p. 348. If the residue is crys-

talline, examine it under the microscope, and then test it according to § 246 or 247, unless the appearance of the crystals should indicate a particular alkaloid. If the residue consists of amorphous rings, dissolve it in absolute alcohol with the aid of a gentle heat, allow the solution to evaporate slowly, observe whether any crystals are thus formed, and then proceed as directed.

*f*. If, on the contrary, the acidified aqueous fluid in *e* has been insufficiently treated with ether, the residue obtained on the evaporation of the ethereal extract will not be pure enough to be tested at once. In this case dissolve it in water slightly acidified with sulphuric acid, filter if necessary, and shake repeatedly with ether (the ethereal solution may contain the remainder of the picrotoxine and digitaline, and is to be treated like the ethereal solution obtained in *c*), mix the aqueous solution with potassa in good excess, and shake repeatedly with ether, as prescribed in *d*. Allow the ethereal extracts to evaporate, and proceed with the residue, thus purified, as in *e*;* mix the aqueous fluid, which may contain the remainder of the morphia, with the fluid obtained in *d*.

*g*. The alkaline fluid obtained in *d*, or in *d* and *f*, which must contain the whole or the greater part of the morphia, is treated as follows:—Add hydrochloric acid to acid reaction, then ammonia in excess, then without delay pure amylic alcohol, and shake.† As morphia is decidedly more readily soluble in warm amylic alcohol than in cold, it is advisable to dip the flask in warm water. Separate the two fluids by means of a funnel, and repeat the extraction with fresh quantities of amylic alcohol. Allow the amylic extracts to evaporate, and test the residue for morphia. If the residue is not pure enough, dissolve it in water acidified with sulphuric acid, filter, shake with warm amylic alcohol, mix the aqueous fluid with ammonia, and shake with amylic alcohol. On evaporating this amylic extract the morphia will remain pure.

*h*. The ethereal extracts obtained in *c*, or in *c* and *f*, have now to be tested for picrotoxine and digitaline. The extracts also contain coloring matters, which are principally present in the first portions. It is therefore advisable to evaporate the first portions apart from the latter portions, and to examine the residues separately.

Warm them with water, and filter the solutions from the insoluble matter, which generally has a resinous character. If the solutions possess an acid reaction, neutralize with some precipitated chalk, evaporate cautiously to dryness, exhaust the residue with ether, allow the extract to evaporate, treat the residue again with

* As it appears that strychnia cannot be obtained pure in this way, FR. JANSSENS recommends (Zeitschr. f. anal. Chem. 4, 48) to mix the solution in dilute tartaric acid containing foreign substances, with finely powdered bicarbonate of soda, so that the fluid may be acidified with free carbonic acid only. If any precipitate is formed, this should be filtered off as quickly as possible. The strychnia is dissolved in the free carbonic acid, and will be precipitated by boiling the filtrate and partially evaporating it. When it has been filtered off and washed, it is dissolved in a small quantity of dilute sulphuric acid (1 : 200), carbonate of potassa is added in excess, and the fluid is shaken with six times its volume of ether, which is then poured off and allowed to evaporate.

† STAS recommended ether only for the extraction of alkaloids, while L. v. USLAR and J. EDMANN (Annal. d. Chem. u. Pharm. 120, 121, and 122, 360) prefer the use of amylic alcohol only. However, it is best to employ both menstrua as directed in the text.

water, and test the aqueous solution thus obtained for digitaline, picrotoxine, and traces of atropine, according to § 247, 1. (In the presence of colchicine the aqueous solution would appear yellow.)

## 2. Methods of detecting Strychnia, based upon the Use of Chloroform.*

### § 249.

#### *a. Rodgers and Girdwood's* Method.†

Digest the substance under examination with dilute hydrochloric acid (1 part of acid to 10 parts of water) and filter; evaporate the filtrate on the water-bath to dryness, extract the residue with spirit of wine, evaporate the solution, treat the residue with water, filter, supersaturate the filtrate with ammonia, add 15 grm. of chloroform, shake, transfer the chloroform to a dish, by means of a pipette, evaporate on the water-bath, moisten the residue with concentrated sulphuric acid, to effect carbonization of foreign organic matters, treat with water, after the lapse of several hours, then filter. Supersaturate the filtrate again with ammonia, and shake it with about 4 grm. of chloroform. Repeat the same operation until the residue left upon the evaporation of the chloroform is no longer charred by sulphuric acid. Transfer the chloroform solution, which leaves a pure residue, drop by drop, by means of a capillary tube, to the same spot on a heated porcelain dish, letting it evaporate, then test the residue with sulphuric acid and chromate of potassa. Rodgers and Girdwood succeeded in detecting by this method so small a quantity of strychnia as the $\frac{1}{2000}$ of a grain.

#### *b.* Method recommended by *E. Prollius.*‡

Boil twice with spirit of wine, mixed with some tartaric acid, evaporate at a gentle heat, filter the residuary aqueous solution through a moistened filter, add ammonia in slight excess, then about 1½ grm. chloroform, shake, free the deposited chloroform thoroughly from the ley, by decanting and shaking with water, mix the chloroform so purified with 3 parts of spirit of wine, and let the fluid evaporate. If there is any notable quantity of strychnia present, it is obtained in crystals.

#### *c.* Method recommended by *R. P. Thomas.*§

Acidify slightly with pure acetic acid‖ (sp. gr. 1·041), and digest for several hours at a gentle heat, then strain, press, filter, add potassa in good excess, and shake with chloroform. Separate the chloroform, wash it from potassa, and evaporate; the strychnia will be found in the residue. The morphia remains in the potassa, and may be precipitated gradually by chloride of ammonium.

* These methods are no doubt useful also for effecting the separation of other alkaloids; however, the deportment of the latter with chloroform has not yet been sufficiently studied.

† Liebig and Kopp's Jahresbericht, 1857, 603. Pharm. Journ. Trans., 16, 497.

‡ Chem. Centrabl., 1857, 231.

§ Zeitschr. f. anal. Chem. 1, 517. This method includes the detection of morphia.

‖ Acetic acid is recommended, as it also dissolves the tannates of strychnia and morphia.

### 3. Method of effecting the Detection of Strychnia in Beer, by *Graham and A. W. Hofmann.**

§ 250.

This method, which is based on the known fact that a solution of a salt of strychnia, when mixed and shaken with animal charcoal, yields its strychnia to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloids. The process is conducted as follows:—

Shake 30 grm. animal charcoal in 1 litre of the aqueous neutral or feebly acid fluid under examination; let the mixture stand for from 12 to 24 hours, with occasional shaking, filter, wash the charcoal twice with water, then boil for half-an-hour with 120 c.c. of spirit of wine of 80—90 per cent., avoiding loss of alcohol by evaporation. Filter the spirit of wine hot from the charcoal, and distil the filtrate; add a few drops of solution of potassa to the residual watery fluid, shake with ether, let the mixture stand at rest, then decant the supernatant ether. The ethereal fluid leaves, upon spontaneous evaporation, the strychnia in a state of sufficient purity to admit of its further examination by reagents.

Macadam† employed the same method in his numerous experiments to detect strychnia in the bodies of dead animals. He treated the comminuted matters with a dilute aqueous solution of oxalic acid in the cold, filtered through muslin, washed with water, heated to boiling, filtered still warm, from the coagulated albuminous matters, shook with charcoal, and proceeded in the manner just described. According to his statements, the residue left by the evaporation of the alcoholic solution was generally at once fit to be tested for strychnia. Where it was not so, he treated the residue again with solution of oxalic acid, and repeated the process with animal charcoal.

### 4. Separation by Dialysis.

§ 251.

The dialytic method devised by Graham, and described in § 8, may also be advantageously employed to effect the separation of alkaloids from the contents of the stomach, intestines, &c. Acidify with hydrochloric acid, and place the matter in the dialyser. The alkaloids, being crystalloids, penetrate the membrane, and are found, for the greater part, after 24 hours, in the outer fluid; from this they may, then, according to circumstances, either be thrown down at once, after concentration by evaporation; or they may be purified by one of the above described methods.

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## II.

## General Plan of the Order in which Substances should be analysed for Practice.

§ 252.

It is not a matter of indifference whether the student, in analysing for the sake of practice, follows no rule or order whatever in the

* Chem. Soc. Quart. Journ., 5, 173. † Pharm. Journ. Trans., 16, 120, 160.

selection of the substances which he intends to analyse, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways, indeed, may lead to the desired end, but one of them will invariably prove the shortest. I will, therefore, here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take 100 compounds, systematically arranged (*see below*), and let him analyze these compounds successively in the order in which they are placed. A careful and diligent examination of these will be amply sufficient to impart to him the necessary degree of skill in practical analysis. When analysing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed for him by a friend who knows their exact composition.

### A. *From* 1 *to* 20.

AQUEOUS SOLUTIONS OF SIMPLE SALTS: *e.g.*, sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analysing substances soluble in water which contain but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, is required.

### B. *From* 21 *to* 50.

SALTS, ETC., CONTAINING ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID (in form of powder): *e.g.*, carbonate of baryta, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, bitartrate of potassa, acetate of copper, sulphate of baryta, chloride of lead, &c. These investigations will serve to teach the student how to make a preliminary examination of a solid substance, by heating in a tube or before the blow-pipe; how to convert it into a proper form for analysis, *i.e.*, how to dissolve or decompose it; how to detect *one* metallic oxide, even in substances *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the base and the acid is required, but it is not necessary to prove that no other bodies are present.

### C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides from each other. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

### D. *From* 66 *to* 80.

DRY MIXTURES OF EVERY DESCRIPTION. A portion of the salts should be organic, another inorganic; a portion of the compounds soluble in water or hydrochloric acid, another insoluble; *e.g.*, mixtures of chloride of sodium, carbonate of lime, and oxide of copper;—of phosphate of magnesia and ammonia, and arsenious acid;—of tartrate of

lime, oxalate of lime, and sulphate of baryta;—of phosphate of soda, nitrate of ammonia, and acetate of potassa, &c.

These investigations will serve to teach the student how to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates of the alkaline earths;—and they will serve as a general introduction to scientific and practical analysis. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

NATIVE COMPOUNDS, ARTICLES OF COMMERCE &c. Mineral and other waters, minerals of every description, soils, potash, soda, alloys, colors, &c.

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## III.

### ARRANGEMENT OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

### § 253.

The manner in which the results of analytical investigations ought to be arranged is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most suitable in this respect.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 1—20.

Colorless fluid of neutral reaction.

| HCl | HS | $NH_4S$ | $NH_4O$, $CO_2$ and $NH_4Cl$ |
|---|---|---|---|
| *no precipitate,* consequently no | *no precipitate,* | *no precipitate,* | *a white precipitate,* |
| AgO | no PbO | no FeO | consequently either |
| $Hg_2O$ | ,, HgO | ,, MnO | BaO, SrO, or CaO, |
| | ,, CuO | ,, NiO | no precipitate by |
| | ,, $BiO_3$ | ,, CoO | solution of sulphate of lime, |
| | ,, CdO | ,, ZnO | consequently |
| | ,, $AsO_3$ | ,, $Al_2O_3$ | LIME. |
| | ,, $AsO_5$ | ,, $Cr_2O_3$ | Confirmation by |
| | ,, $SbO_5$ | | $\overline{O}$ |
| | ,, $SnO_2$ | | |
| | ,, SnO | | |
| | ,, $AuO_3$ | | |
| | ,, $PtO_2$ | | |
| | ,, $Fe_2O_3$ | | |

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 21—50.

White powder, fusing in the water of crystallization upon application of heat, then remaining unaltered—soluble in water—reaction neutral.

| HCl | HS | $NH_4S$ | $NH_4O, CO_2$, and $NH_4Cl$ | $2NaO, HO, PO_5$ and $NH_4O$ |
|---|---|---|---|---|
| *no precipitate.* | *no precipitate.* | *no precipitate.* | *no precipitate.* | *a white precipitate,* consequently MAGNESIA. |

The detected base being MgO, and the analysed substance being soluble in water, the acid can only be Cl, I, Br, $SO_3$, $NO_5$, $\dot{A}$, &c. The preliminary examination has proved the absence of the organic acids and of nitric acid.

BaCl produces a white precipitate which HCl fails to dissolve; consequently SULPHURIC ACID.

A white powder, acquiring a permanent yellow tint upon application of heat, without forming a sublimate, and without emitting visible fumes marked by acid or alkaline reaction. Before the blowpipe, a malleable metallic globule, and yellow incrustation, with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in that acid, readily soluble in nitric acid to a colorless fluid.

| H Cl | H S | N H S | | $NH_4O, CO_2$ | No fixed residue upon evaporation. | Hydrate of lime has failed to evolve ammonia. |
|---|---|---|---|---|---|---|
| White precipitate, insoluble in an excess, quite soluble in hot water; $SO_3$ producing a white precipitate in the solution: LEAD. | Black precipitate, insoluble in sulphide of ammonium, readily soluble in nitric acid. $SO_3$ produces a white precipitate: LEAD. Examination for Cu, Bi, and Cd: results negative. | White precipitate; ammonia, applied by itself, produces no precipitate; solution of precipitate in hydrochloric acid remains clear upon addition of soda in excess. | | White precipitate; upon dissolving this in hydrochloric acid, and adding solution of sulphate of lime to the fluid, a white precipitate forms after some time: STRONTIA. Precipitation and boiling with sulphate of ammonia, filtrate tested for lime with $\bar{O}$: results negative. | | |
| | | $NH_4Cl$ no precipitate. | H S white precipitate: ZINC. | | | |

Of the acids CARBONIC ACID has already been found. Of the remaining acids the following cannot be present:

The preliminary examination has proved the absence of organic acids and nitric acid.

$ClO_5$ cannot be present, because the substance is entirely insoluble in water.

S and $SO_3$ not, because the substance is readily soluble in nitric acid.

$CrO_3$ not, as the nitric acid solution is colorless.

$PO_5$, $SiO_2$, HF, and $\bar{O}$ not, because the solution filtered from the sulphide of lead was not precipitated by simple addition of ammonia.

$BO_3$ might be present in trifling quantity; the examination for it gave a negative result.

Cl, I, Br might be present in the form of basic compounds of lead. However, nitrate of silver has produced no precipitate in the nitric acid solution; accordingly, they cannot be present.

The substance contains, therefore { bases: oxide of lead, oxide of zinc, strontia. / acids: carbonic acid.

IV.

# TABLE

OF THE

## MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES TREATED OF IN THE PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS TO WHICH THEY RESPECTIVELY BELONG ACCORDING TO THEIR SOLUBILITY

## IN WATER, IN HYDROCHLORIC ACID, IN NITRIC ACID, OR IN NITROHYDROCHLORIC ACID.

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### § 254.

#### PRELIMINARY REMARKS.

The class to which the several compounds respectively belong according to their solubility in water or acids (see § 179), is expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid; 3 or III a substance insoluble in water, in hydrochloric acid, and in nitric acid. For those substances which stand as it were on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance sparingly soluble in water, but soluble in hydrochloric acid or nitric acid; 1—3 a body sparingly soluble in water, and of which the solubility is not notably increased by the addition of acids; and 2—3 a substance insoluble in water, and sparingly soluble in acids. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The Roman figures denote officinal and more commonly occurring compounds.

The haloid salts and sulphur compounds are placed in the columns of the corresponding oxides. The salts given are, as a general rule, the neutral salts; the basic, acid, and double salts, if officinal, are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts refer to these.

| | KO | NaO | $NH_4O$ | BaO | SrO | CaO | MgO | $Al_2O_3$ | $Cr_2O_3$ | ZnO | MnO | NiO | Co |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | I | I | I | 1 | I-II | II | II | II & III | II | $2_{17}$ | II | II |
| $CrO_3$ | $I_1$ | 1 | 1 | 2 | 1-2 | 1-2 | 1 | | 2 | 1 | 1 | 2 | 2 |
| $SO_3$ | $I_{2\cdot15\cdot15}$ | I | $I_{14\cdot20\cdot20}$ | III | III | I-III | I | $I_{13\cdot14}$ | I & $II_{15}$ | I | I | I | I |
| $PO_5$ | 1 | $I_8$ | $I_{8\cdot12}$ | 2 | 2 | $II_{11}$ | $2_{12}$ | 2 | 2 | 2 | 2 | 2 | 2 |
| $BO_3$ | $I_3$ | 1 | $I_9$ | 2 | 2 | 2 | 1-2 | 2 | 2 | 2 | 2 | 2 | 2 |
| $\overline{O}$ | $I_4$ | I | I | 2 | 2 | II | 2 | 2 | 1-2 | 2 | 1-2 | 2 | 2 |
| F | 1 | 1 | I | 2-3 | 2-3 | II-III | 2-3 | 1 | 1 | 1-2 | 2 | 1-2 | 1-3 |
| $CO_2$ | $I_5$ | $I_{10}$ | I | II | II | II | II | | | II | II | II | II |
| $SiO_2$ | I | I | | 2 | 2 | 2 | 2 | 2-3 | 2 | 2 | 2 | 2 | 2 |
| Cl | $I_{27}$ | $I_{25}$ | $I_{21\cdot28}$ | I | I | I | I | 1 | I & III | I | I | I | I |
| Br | I | I | 1 | 1 | 1 | 1 | 1 | 1 | 1 & 3 | 1 | 1 | 1 | 1 |
| I | I | 1 | I | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Cy | I | 1 | 1 | 1-2 | 1 | 1 | 1 | | 2 | II | 2 | 2-3 | 2-3 |
| Cfy | I | 1 | 1 | 1-2 | 1 | 1 | 1 | | | II-III | 2 | 3 | 3 |
| Cfdy | I | 1 | 1 | | | 1 | 1 | | | 2 | 3 | 3 | 3 |
| S | I | I | I | I | 1 | I-$II_{45}$ | 2 | 2 | 2-3 | $II_{16}$ | II | $2_{18}$ | $2_{18}$ |
| $NO_5$ | I | I | I | I | I | 1 | 1 | 1 | I | 1 | 1 | 1 | I |
| $ClO_5$ | I | 1 | 1 | 1 | I | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\overline{T}$ | $I_{5\cdot6\cdot7}$ $_{22\cdot46}$ | $I_7$ | $I_6$ | 2 | 2 | II | 1-2 | 1 | 1 | 2 | 1-2 | 2 | 1 |
| $\overline{Ci}$ | 1 | 1 | 1 | 2 | 2 | 1-2 | 1 | 1 | 1 | 1-2 | 2 | 1 | 1 |
| $\overline{Ma}$ | 1 | 1 | 1 | 1&2 | 1 | 2 | 1 | 1 | | 1 | 1 | | |
| $\overline{Su}$ | 1 | 1 | 1 | 1-2 | 1-2 | 1-2 | 1 | 1-2 | | 1-2 | 1 | 1 | 1-3 |
| $\overline{Bz}$ | 1 | 1 | 1 | 1 | | 1 | 1 | | | | 1 | | |
| $\overline{A}$ | I | I | I | I | 1 | I | 1 | I | 1 | I | 1 | 1 | 1 |
| $\overline{Fo}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $AsO_3$ | I | 1 | 1 | 2 | 2 | 2 | 2 | | | | 2 | 2 | 2 |
| $AsO_5$ | I | I | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | KO | NaO | $NH_4O$ | BaO | SrO | CaO | MgO | $Al_2O_3$ | $Cr_2O_3$ | ZnO | MnO | NiO | Co |

## NOTES TO TABLE OF SOLUBILITY.

1. Bichromate of potassa I.
2. Bisulphate of potassa I.
3. Tartarized borax I.
4. Binoxalate of potassa I.
5. Bitartrate of potassa I.
6. Tartrate of ammonia and potassa I.
7. Tartrate of soda and potassa I.
8. Phosphate of soda and ammonia I.

| $Fe_2O_3$ | Ag O | Pb O | $Hg_2O$ | Hg O | Cu O | $Bi O_3$ | Cd O | $Au O_3$ | $Pt O_2$ | Sn O | $Sn O_2$ | $Sb O_5$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| II | 2 | $II_{24}$ | II | II | II | 2 | 2 | | 2 | 2 | 2 & 3 | $II_{42}$ | |
| 1 | 2 | II-III | 2 | 1-2 | 1 | 2 | 2 | | | 2 | | 2 | $CrO_3$ |
| I | I-II | II-III | 1-2 | $1_{27}$ | $I_{30}$ | 1 | I | | 1 | 1 | | 2 | $SO_3$ |
| II | 2 | 2 | 2 | 2 | 2 | 2 | 2 | | | 2 | 2 | 1-2 | $PO_5$ |
| 2 | 2 | 2 | | | 2 | 2 | 1-2 | | | 2 | | | $BO_3$ |
| 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | | 1 | 2 | 1 | 2 | $\overline{U}$ |
| 1 | 1 | 2 | | 1-2 | 2 | 1 | 1-2 | | | 1 | 1 | 1 | F |
| | 2 | II | 2 | 2 | II | 2 | 2 | | | | | | $CO_2$ |
| 2 | | 2 | | | 2 | | 2 | | | | | | $SiO_2$ |
| $I_{21}$ | III | I-III | II-III | $I_{28}$ | I | I-$II_{28}$ | I | $I_{25}$ | $I_{27\cdot28}$ | I | $I_{40}$ | I-$II_{43}$ | Cl |
| 1 | 3 | 1-3 | 2-3 | 1 | 1 | 1-2 | I | 1 | 1 | | | 1-2 | Br |
| 1 | 3 | I-II | II | II | 1 | 2 | I | 2 | 3 | 1 | 1 | 1-2 | I |
| | III | 2 | | I | 2 | | 2 | I | 1 | | | | Cy |
| III | 3 | 2 | | | 3 | | | | | 3 | 3 | | Cfy |
| 1 | 3 | 1-2 | | | | | | | | 3 | | | Cfdy |
| 2 | $2_{23}$ | II | II | $I_{29}$ | $2_{31}$ | 2 | II | $2_{26}$ | $2_{39}$ | $2_{41}$ | $2_{41}$ | $II_{44\cdot45}$ | S |
| 1 | I | I | $I_{26}$ | I | I | $I_{34}$ | 1 | | 1 | | | | $NO_5$ |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | | 1 | | | $ClO_5$ |
| $I_{22}$ | 2 | 2 | 1-2 | 2 | 1 | 2 | 1-2 | | | 2 | | $2_{46}$ | $\overline{T}$ |
| I | 2 | 2 | 2 | 1-2 | 1 | | 2 | | | | | | $\overline{Ci}$ |
| I | 1-2 | 1-2 | 2 | 1-2 | 1 | | | | | 1 | 1 | | $\overline{Ma}$ |
| 2 | 2 | 2 | 2 | 1-2 | 1-2 | | 1 | | | | 2 | | $\overline{Su}$ |
| 2 | 1-2 | 2 | 2 | 1-2 | 2 | | 1 | | | | | | $\overline{Bz}$ |
| I | 1 | $I_{25}$ | 1-2 | 1 | $I_{33}$ | 1 | 1 | | | 1 | 1 | | $\overline{A}$ |
| I | 1 | 1-2 | 1 | 1 | 1 | 1 | 1 | | | 1 | | | $\overline{Fo}$ |
| 2 | 2 | 2 | 2 | 2 | II | | | | | | | 2 | $AsO_3$ |
| 2 | 2 | 2 | 2 | 2 | 2 | 2 | | | | | 2 | 2 | $AsO_5$ |
| $Fe_2O_3$ | Ag O | Pb O | $Hg_2O$ | Hg O | Cu O | $Bi O_3$ | Cd O | $Au O_3$ | $Pt O_2$ | Sn O | $Sn O_2$ | $Sb O_5$ | |

9. Biborate of soda I.
10. Bicarbonate of soda I.
11. Basic phosphate of lime II.
12. Phosphate of ammonia and magnesia II.
13. Sulphate of alumina and potassa I.
14. Sulphate of alumina and ammonia I.
15. Sulphate of sesquioxide of chromium and potassa I.
16. Sulphide of zinc readily in nitric acid, rather difficultly in hydrochloric acid.
17. Peroxide of manganese readily in hydrochloric acid, not in nitric acid.

18. Sulphide of nickel rather readily in nitric acid, with great difficulty in hydrochloric acid.
19. Sulphide of cobalt like sulphide of nickel.
20. Sulphate of protoxide of iron and ammonia I.
21. Chloride of arsenic and ammonium I.
22. Tartrate of sesquioxide of iron and potassa I.
23. Sulphide of silver in nitric acid only.
24. Minium is converted by hydrochloric acid into chloride of lead, by nitric acid into protoxide, which dissolves in excess of acid, and into brown peroxide, which is insoluble in nitric acid.
25. Trisacetate of lead I.
26. Mercurius solubilis Hahnemanni II.
27. Basic sulphate of oxide of mercury II.
28. Double chloride and amide of mercury II.
29. Sulphide of mercury, not in hydrochloric acid, not in nitric acid; but in warm aqua regia.
30. Sulphate of copper and ammonia I.
31. Sulphide of copper difficultly in hydrochloric acid, readily in nitric acid.
32. Basic acetate of copper partially in water, completely in acids.
33. Basic chloride of bismuth II.
34. Basic nitrate of bismuth II.
35. Chloride of sodium and gold I.
36. Sulphide of gold, not in hydrochloric acid nor in nitric acid, but in warm aqua regia.
37. Potassio-bichloride of platinum 1-3.
38. Ammonio-bichloride of platinum I-III.
39. Sulphide of platinum, not in hydrochloric acid, scarcely in boiling nitric acid, but in warm aqua regia.
40. Chloride of ammonium and tin I.
41. Protosulphide and bisulphide of tin in warm hydrochloric acid, converted by nitric acid into binoxide, which is insoluble in excess of the acid. Sublimed bisulphide of tin only in warm aqua regia.
42. Teroxide of antimony in hydrochloric acid, not in nitric acid.
43. Basic chloride of antimony II.
44. Sulphide of antimony in hydrochloric acid, particularly on heating; decomposed but only very partially dissolved by nitric acid.
45. Sulphide of antimony and calcium I-II.
46. Tartrate of antimony and potassa I.

# INDEX.


ACETATES, properties, 218
— reactions, 218
Acetic acid, detection, 220
— properties, 218
— purification, 40
— reactions, 218
— tests of purity, 39
— uses as reagent, 40
Acids, grouping, 170
Albumen on metaphosphoric acid, 180
— on phosphoric acid, 180
— on pyrophosphoric acid, 180
Alcohol, preparation of absolute, 35
— tests of purity, 35
— uses as reagent, 36
— on acetates, 219
— on chromates, 172
— on formates, 220
— on osmic acid, 141
Alkalies, properties, 81
Alkaline earths, properties, 89
Alloys, analysis, 235
— preliminary examination, 231
Alumina, decomposition of insoluble compounds, 99
— properties, 99
— reactions, 99
— separation from sesquioxide chromium, 102
Alumina carbonate, properties, 100
Alumina phosphate, properties, 100
Alumina salts, properties, 99
Aluminium, properties, 99
Ammonia, detection of minute quantities, 87
— NESSLER'S test, 87
— preparation of solution, 51
— properties, 85
— reactions, 85, 87
— separation from other alkalies, 86
— tests of purity, 51
— uses as reagent, 51
— on alumina salts, 100
— on antimony salts, 150
— on baryta salts, 90
— on beryllia salts, 103
— on bismuth salts, 136
— on cadmium salts, 138
— on cerium salts, 106
— on chromium salts, 101
— on cobalt salts, 118
Ammonia, on copper salts, 134
— on didymium salts, 107
— on gold salts, 148
— on hydrofluosilicic acid, 176
— on indium salts, 126
— on iron protoxide salts, 120
— on iron sesquioxide salts, 121
— on lanthanium salts, 107
— on lead salts, 130
— on lime salts, 93
— on magnesia salts, 95
— on manganese salts, 114
— on mercury chloride, 87
— on mercury chloride and soda carbonate, 87
— on mercury and potassium iodide, 87
— on mercury oxide salts, 133
— on mercury subsalts, 129
— on nickel salts, 116
— on niobic acid, 110
— on osmic acid, 141
— on palladium salts, 140
— on rhodium salts, 140
— on silver salts, 128
— on strontia salts, 91
— on tantalic acid, 109
— on thallium protoxide salts, 125
— on thoria salts, 103
— on tin binoxide salts, 148
— on tin protoxide salts, 146
— on titanic acid, 108
— on uranium salts, 124
— on yttria salts, 105
— on zinc salts, 112
— on zirconia salts, 104
Ammonia bitartrate, properties, 85
Ammonia carbonate, preparation of solution, 58
— tests of purity, 58
— uses as reagent, 58
— on alumina salts, 100
— on antimony salts, 150
— on baryta salts, 90
— on beryllia salts, 103
— on bismuth salts, 136
— on cadmium salts, 138
— on cerium salts, 106
— on chromium salts, 101
— on didymium salts, 107
— on indium salts, 126

Ammonia carbonate, on lanthanium salts, 107
— on lime salts, 93
— on magnesia salts, 96
— on strontia salts, 91
— on thallium protoxide salts, 125
— on thoria salts, 103
— on tin binoxide salts, 148
— on tin protoxide salts, 146
— on uranium salts, 124
— on yttria salts, 105
— on zinc salts, 112
— on zirconia salts, 104
Ammonia molybdate, preparation, 60
— uses as reagent, 61
— on arsenic acid, 179
— on phosphoric acid, 179
— on pyrophosphoric acid, 180
— on silicic acid, 179
Ammonia oxalate, preparation, 56
— preparation of solution, 57
— tests of purity, 57
— uses as reagent, 57
— on baryta salts, 90
— on indium salts, 126
— on lime salts, 93
— on magnesia salts, 96
— on strontia salts, 92
Ammonia phosphomolybdate, properties, 179
Ammonia salts, properties, 85
Ammonia vanadate, properties, 127
Ammonium chloride, preparation of solution, 61
— purification, 61
— tests of purity, 61
— uses as reagent, 61
— on iridium salts, 166
— on platinum salts, 144
— on ruthenium salts, 141
— on silicates, 189
— on vanadates, 127
Ammonium and platinum chloride, properties, 85
Ammonium sulphide, action of air, 54
— action of acid on yellow, 55
— nature of yellow, 55
— preparation, 54
— tests of purity, 55
— uses as reagent, 55
— on antimony salts, 150
— on arsenic acid, 162
— on arsenious acid, 155
— on berylla salts, 103
— on bismuth salts, 136
— on chromates, 172
— on cobalt salts, 117
— on cyanides, 198
— on gold salts, 143
— on indium salts, 126
— on iridium salts, 166
— on iron protoxide salts, 119
— on iron sesquioxide salts, 121
— on manganese salts, 113
— on mercury subsalts, 129
— on molybdic acid, 167
Ammonium sulphide, on nickel salts, 115
— on niobic acid, 110
— on palladium salts, 140
— on platinum salts, 144
— on ruthenium salts, 142
— on silver salts, 128
— on tantalic acid, 109
— on thallium protoxide salts, 125
— on thoria salts, 103
— on tin binoxide salts, 148
— on tin protoxide salts, 146
— on titanic acid, 108
— on tungstates, 168
— on uranium salts, 124
— on vanadates, 126
— on vanadic acid, 126
— on yttria salts, 105
— on zinc salts, 112
— on zirconia salts, 104
Analysis, course, 225
— remarks on course, 327
— arrangement of results, 375
— of simple compounds when soluble in water, 236
— of simple compounds when soluble in acids, 245
— of simple compounds when insoluble, 249
— of complex compounds when soluble, 251
— of complex compounds when insoluble, 278
Antimonates, properties, 149
Antimonetted hydrogen, properties, 151
— separation from arsenetted hydrogen, 164
— on silver nitrate, 164
Antimonic acid, properties, 149
— separation from antimony teroxide, 165
Antimony, properties, 148
— reactions, 149
— separation from tin and arsenic, 163
Antimony oxides, properties, 149
Antimony salts, properties, 149
Antimony teroxide, separation from antimonic acid, 165
Antimony tersulphide, properties, 150
Apparatus, list, 31
Aqua regia, nature, 42
— preparation, 42
— uses as reagent, 43
Arsenates, properties, 161
Arsenetted hydrogen, properties, 156
— separation from antimonetted hydrogen, 164
— on silver nitrate, 164
Arsenic, detection in poisoning cases, 308
— garlic odor, 161
— Marsh's test, 156
— properties, 152
— Reinsch's test, 155
— separation from tin and antimony, 163
Arsenic acid, properties, 161
— reactions, 161
— separation from arsenious acid, 165

Arsenic pentasulphide, formation, 162
— separation from arsenic tersulphide, 165
Arsenic tersulphide, properties, 153
— separation from arsenic pentasulphide, 165
Arsenious acid, properties, 153
— best way to identify when pure, 158
— reactions, 153
— separation from arsenic acid, 165
Arsenites, properties, 153
Ash, analysis, 323
Atropine, detection, 361, 364, 366, 369
— properties, 360
— reactions, 361
— salts, properties, 360

BARIUM chloride, preparation from heavy-spar, 64
— preparation from witherite, 64
— preparation of solution, 64
— tests of purity, 64
— uses as reagent, 64
— on benzoates, 217
— on borates, 181
— on carbonates, 189
— on hydrofluoric acid, 183
— on hydrofluosilicic acid, 176
— on hypophosphites, 205
— on hyposulphites, 174
— on iodates, 174
— on oxalates, 182
— on perchlorates, 209
— on phosphoric acid, 177
— on phosphorous acid, 187
— on pyrophosphoric acid, 180
— on selenious acid, 169
— on succinates, 216
— on sulphates, 175
— on sulphites, 173
— on tungstates, 168
— on vanadates, 126
Barium fluoride, properties, 183
Barium silicofluoride, properties, 90
Baryta, preparation of crystals, 51
— preparation of dry hydrate, 75
— preparation of solution, 52
— properties, 89
— reactions, 90
— separation from other alkaline earths, 97
— and strontia, detection of minute quantities in presence of lime, 98
— tests of purity, 52
— uses as reagent, 52
— uses as flux, 75
— on carbonic acid, 188
— on magnesia salts, 95
Baryta acetate ou citrates, 212
Baryta borate, properties, 181
Baryta carbonate, preparation, 65
— properties, 90
— tests of purity, 65
— uses as reagent, 65
— on alumina salts, 100
Baryta carbonate, on beryllа salts, 103
— on cerium salts, 106
— on chromium salts, 101
— on cobalt salts, 118
— on didymium salts, 107
— on indium salts, 126
— on iron protoxide salts, 120
— on iron sesquioxide salts, 122
— on lanthanium salts, 107
— on manganese salts, 114
— on nickel salts, 116
— on thoria salts, 103
— on titanic acid, 108
— on uranium salts, 124
— on yttria salts, 105
— on zinc salts, 112
— on zirconia salts, 104
Baryta chromate, properties, 91
Baryta citrate, properties, 212
Baryta iodate, properties, 174
Baryta nitrate, preparation, 65
— preparation of solution, 65
— tests of purity, 65
— uses as reagent, 65
Baryta oxalate, properties, 90, 182
Baryta phosphate, properties, 90
Baryta pyrophosphate, properties, 180
Baryta salts, properties, 90
Baryta selenite, properties, 169
Baryta sulphate, properties, 90
Bases, groups, 81
— of group 1, properties, 81
— of group 2, properties, 89
— of group 3, properties, 98
— of group 4, properties, 111
— of group 5, properties, 127
— of group 6, properties, 142
— oxygen, classification, 48, 81
— oxygen, definition, 48
— oxygen, properties, 48
— sulphur, definition, 48
— sulphur, properties, 48
Benzoates, properties, 217
— reactions, 217
Benzoic acid, detection, 217
— properties, 217
— reactions, 217
Berylla, detection in analytical course, 339, 340
— occurrence, 103
— properties, 103
— reactions, 103
Berylla carbonate, properties, 103
Berylla salts, properties, 103
Berzelius lamp, 19
Bismuth, properties, 136
— purification from arsenic, 53
— reactions, 136
— separation from other members of Gr. 5, Div. 2, 138
Bismuth, basic chloride, properties, 137
Bismuth, basic nitrate, 53
Bismuth carbonate, properties, 136
Bismuth chromate, properties, 136
Bismuth hydrate, preparation, 53

Bismuth hydrate, tests of purity, 54
— uses as reagent, 54
Bismuth oxides, properties, 136
Bismuth and potassium iodide, as reagent for alkaloids, 344
— preparation, *footnote*, 344
Bismuth salts, properties, 136
Bismuth tersulphide, properties, 136
Blowpipe, 15
— flame, 16
Boiling, action on titanic acid solution, 108
Boracic acid, detection, 186
— loss on evaporation, 186
— properties, 180
— reactions, 181
Borates, properties, 180
Borax, tests of purity, 77
— uses as flux, 78
Borax bead, testing with, 78
— with cerium salts, 106
— with chromium salts, 102
— with cobalt salts, 119
— with copper salts, 135
— with didymium oxide, 107
— with erbium oxide, 106
— with iron salts, 120
— with manganese salts, 115
— with nickel salts, 116
— with uranium salts, 124
— with vanadic acid, 127
— with yttria, 105
— and copper oxide with tin salts, 147
Boron fluoride, formation, 182
Bromides, reactions, 193
— insoluble, decomposition, 194
Bromine, detection, 202
— properties, 193
— reactions, 193
Brucine, detection, 361, 364, 366, 369
— properties, 358
— reactions, 358
— on chlorates, 208
— on nitrates, 207
Brucine salts, properties, 358
Bunsen flame, parts, 23
Bunsen lamp, 20
— improved, 22
Butyric acid, detection, 221
— properties, 221
— reactions, 221

CADMIUM, properties, 137
— reactions, 137
— separation from other members of Gr. 5, Div. 2, 138
Cadmium carbonate, properties, 138
Cadmium oxide, properties, 137
Cadmium and potassium iodide, as reagent for alkaloids, 344
— preparation, *footnote*, 344
Cadmium salts, properties, 137
Cadmium sulphide, properties, 138
Cæsia, detection in analytical course, 340
Cæsia, rubidia, and lithia, detection in presence of much potassa and soda, 89
— and rubidia, difference from potassa, 87
— distribution, 87
— reactions, 87
Cæsia alum, solubility, 88
Cæsia bitartrate, solubility, 88
Cæsia carbonate, solubility in alcohol, 88
Cæsium and platinum chloride, solubility, 87
Calcium, reactions, 93
Calcium chloride, preparation, 66
— preparation of solution, 66
— tests of purity, 66
— uses as reagent, 66
— on carbonates, 189
— on citrates, 211
— on hydrofluoric acid, 184
— on hypophosphites, 205
— on malates, 213
— on phosphorous acid, 187
— on racemates, 215
— on succinates, 216
— on tartrates, 210
— on tungstates, 168
Calcium fluoride, properties, 184
— uses as reagent, 75
— and potassa bisulphate with borates, 181
Calcium salts, properties, 93
Carbolic acid and sulphuric acid on nitrates, 207
Carbon, properties, 187
Carbonates, properties, 188
— reactions, 188
Carbonic acid, detection, 191
— properties, 188
— reactions, 188
— on soda niobate, 110
— on tantalates, 110
Carbon bisulphide, tests of purity, 36
— uses as reagent, 36
— as solvent for bromine, 193
— as solvent for iodine, 196, 203
Cassius, purple, 143
Cerite, decomposition, 106
Cerium, detection in analytical course, 339, 340
— occurrence, 106
— reactions, 106
— separation from lanthanium and didymium, 107
Cerium oxides, properties, 106
Cerium protoxide and potassa sulphate, properties, 106
Cerium salts, properties, 106
Charcoal, 18
Chlorates, properties, 207
— reactions, 207
Chloric acid, detection, 208
— properties, 207
— reactions, 207
Chlorides, insoluble, decomposition, 192
— properties, 192
— reactions, 192
Chlorine, detection, 202, 203

**Chlorine, detection of free, 191**
— preparation, 42
— preparation of solution, 42
— preservation of solution, 42
— properties, 191
— purification, 42
— reactions, 192
— uses as reagent, 42
— on bromides, 193
— on cerium salts, 106
— on iodides, 196
— on iridium and sodium chloride, 166
— on niobic acid and charcoal, 110
— on osmium, 141
— on sulphites, 173
— on tantalic acid and charcoal, 109
— on titanic acid and charcoal, 109
Chlorites, properties, 205
— reactions, 205
Chlorochromic acid, properties, 192
Chloroform, tests of purity, 36
— uses as reagent, 36
Chlorous acid, properties, 205
— reactions, 205
Chromates, insoluble, decomposition, 172
— properties, 171
— reactions, 171
Chrome iron stone, decomposition, 281
Chromic acid, detection, 173
— detection of minute quantities, 173
— properties, 171
— reactions, 171
— on hyposulphites, 174
— on sulphites, 173
Chromium, detection of minute quantities, 173
— reactions, 101
— separation from aluminium, 102
Chromium carbonate, properties, 101
Chromium chromate, formation, 172
Chromium salts, properties, 101
Chromium sesquioxide, properties, 101
— reactions, 101
— separation from alumina, 102
Cinchonine, detection, 355, 364, 366
— properties, 354
— reactions, 354
Cinchonine salts, properties, 354
Citrates, properties, 211
— reactions, 211
Citric acid, detection, 214
— properties, 211
— reactions, 211
Cobalt, properties, 117
— reactions, 117
— separation from other members of Gr. 4, 122
Cobalt ferricyanide, properties, 118
Cobalt ferrocyanide, properties, 118
Cobalticyanide potassium, formation, 118
Cobalt nitrate, preparation, 79
— tests of purity, 79
— uses as reagent, 79
— with alumina salts, 100
— with beryllia salts, 103
Cobalt nitrate, with zinc salts, 113
Cobalt oxide, properties, 117
Cobalt and potassium cyanide, properties, 118
Cobalt salts, properties, 117
Cobalt sesquioxide, properties, 117
Cobalt sesquioxide and potassa nitrite, 118
Cobalt sulphide, properties, 117
Colloids, definition, 10
Condenser, LIEBIG's, 12
Conine, detection, 348
— properties, 347
— reactions, 348
Conine salts, properties, 347
Copper, properties, 133
— reactions, 134
— separation from other members of Gr. 5, Div. 2, 138
— uses as reagent, 53
— on arsenic acid, 162
— on arsenious acid, 155
— on mercury salts, 129
— on molybdic acid, 167
— on nitric acid, 206
— on selenious acid, 169
— on sulphurous acid, 173
Copper arsenide, properties, 155
Copper carbonate, basic, properties, 134
Copper ferrocyanide, properties, 135
Copper oxide, properties, 133
Copper salts, properties, 134
Copper subiodide, properties, 195
Copper subsulphocyanide, properties, 135
Copper sulphate, preparation, 69
— preparation of solution, 69
— tests of purity, 69
— uses as reagent, 70
— on arsenic acid, 162
— on arsenious acid, 155
— on arsenious acid and potassa, 155
— on ferricyanides, 200
— on ferrocyanides, 199
— on iodides and sulphurous acid, 195
Copper sulphide, properties, 134
Crucibles, platinum, rules for using, 14
Crystallization, 5
Crystalloids, definition, 9
Cyanides, insoluble, analysis, 282
— properties, 197
— reactions, 197
Cyanogen, detection, 202
— detection in mercury cyanide, 199
— properties, 197
— reactions, 197

DAHLIA paper, preparation, 72
— uses as reagent, 72
Decantation, 8
— washing by, 9
Deflagration, 15
— of chlorates, 207
— of nitrates, 206
Dialyser, 10

Dialysis, 9
Didymium, detection in anal. course, 339
— occurrence, 107
— oxide, properties, 107
— oxide, reactions, 107
— salts, properties, 107
Digitaline, detection, 364, 366, 369
— properties, 362
— reactions, 362
Distillation, 12

EARTHS, alkaline, properties, 89
Erbium, detection in analytical course, 339
— occurrence, 105
— reactions, 105
— separation from yttrium, 106
— basic nitrate, properties, 105
— oxalate, properties, 105
— oxide, properties, 105
— salts, properties, 105
— sulphate, properties, 105
Etching test for fluorine, 184
Ether, tests of purity, 36
— uses as reagent, 36
— acetic, formation, 219
Evaporation, 11
Excess, meaning, 33
Exercises, plan, 373

FERRICYANIDES, insoluble, decomposition, 200
— properties, 200
Ferricyanogen, reactions, 200
Ferrocyanides, insoluble, decomposition, 199
— properties, 199
Ferrocyanogen, reactions, 199
Filtering paper, 7
— purification, 8
Filter stand, 8
Filters, washing, 8
Filtration, 7
Flame, parts, 16
— oxidizing, 17
— reducing, 17
Flame coloration, examination, 26
— of baryta salts, 91
— of baryta salts with alcohol, 91
— of boracic acid with alcohol, 181
— of boracic acid with potassa bisulphate and calcium fluoride, 181
— of cæsium salts, 87
— of chlorides with alcohol, 181
— of copper salts, 135
— of copper salts with alcohol, 181
— of indium salts, 126
— of lime salts, 94
— of lime salts with alcohol, 94
— of lithia salts, 88
— of osmium salts, 141
— of potassa salts, 83
— of potassa salts with alcohol, 83
— of rubidium salts, 87
Flame coloration of soda salts, 84
— of soda salts with alcohol, 84
— of strontia salts, 92
— of strontia salts with alcohol, 92
— of thallium salts, 125
Flame reactions, BUNSEN'S, 24
— of antimony, 152
— of bismuth, 137
— of cadmium, 138
— of cobalt, 119
— of gold, 144
— of iron, 120
— of lead, 131
— of manganese, 117
— of selenium, 169
— of silver, 128
— of tellurium, 168
— of zinc, 113
Fluorides, properties, 183
Fluorine, detection in silicates, 185
— reactions, 183
— in sulphuric acid, *footnote*, 184
Formates, properties, 219
— reactions, 219
Formic acid, detection, 220
— reactions, 219
Fulminating gold, 143
Funnels, 8
Fusion, 14

GALLS on molybdic acid, 167
— on tantalic acid, 110
— on titanic acid, 108
— on tungstates of alkalies, 168
— on vanadates, 127
— on vanadic acid, 126
Gauze plate, 21
Georgina paper, preparation, 72
— uses as reagent, 72
Gold, properties, 143
— reactions, 143
— separation from platinum, 145
Gold chloride, preparation, 71
— uses as reagent, 71
— on bromides, 194
— on tin protoxide salts, 143, 146
Gold, fulminating, 143
— oxides, properties, 143
— protosulphide, properties, 143
— salts, properties, 143
— sulphide, properties, 143
Guaiacum on chromic acid, 173
— and copper sulphate on hydrocyanic acid, 199

HYDRIODIC acid, detection, 202
— properties, 195
— reactions, 195
Hydrobromic acid, detection, 202
— properties, 193
— reactions, 193
Hydrochloric acid, detection, 202, 203
— preparation, 40

Hydrochloric acid, properties, 192
— purification, 41
— reactions, 192
— tests of purity, 41
— uses as reagent, 41
— on borates, 181
— on carbonates, 188
— on chlorates, 208
— on chromates, 172
— on cyanides, 197
— on hyposulphites, 174
— on lead salts, 131
— on mercury subsalts, 129
— on perchlorates, 209
— on silicates, 189
— on silver salts, 128
— on sulphides, 200
— on sulphites, 173
— on tantalates, 109
— on thallium protoxide salts, 125
— on thallium trioxide salts, 125
— on tungstates, 167
— and ether on ferrocyanides, 199
Hydrocyanic acid, detection, 202
— detection in poisoning cases, 316
— properties, 197
— reactions, 197
Hydroferricyanic acid, properties, 200
— reactions, 200
Hydroferrocyanic acid, properties, 199
— reactions, 199
Hydrofluoric acid, detection, 187
— properties, 183
— reactions, 183
— on niobic acid, 110
— on silicates, 190
— on tantalic acid, 109
— on thoria salts, 103
— on yttria salts, 105
— on zirconia salts, 104
Hydrofluosilicic acid, preparation, 43
— properties, 176
— reactions, 176
— tests of purity, 43
— uses as reagent, 43
— on borates, 182
— on baryta salts, 90
— on lime salts, 93
— on magnesia salts, 96
— on strontia salts, 92
Hydrogen on niobic acid, 110
— on osmium salts, 141
— on rhodium salts, 140
— on tantalic acid, 109
Hydrogen binoxide, preparation, *footnote*, 172
— on chromates, 172
— on vanadates, 127
Hydrosulphuric acid, Brugnatelli's apparatus, 45
— Mohr's apparatus, 47
— Pohl's apparatus, 47
— detection, 202
— preparation, 44
— preparation of solution, 47
— preservation of solution, 47
Hydrosulphuric acid, properties, 200
— reactions, 201
— tests of purity, 47
— uses as reagent, 48
— on antimonic acid, 150
— on antimony salts, 150
— on arsenic acid, 161
— on arsenious acid, 153
— on bismuth salts, 136
— on cadmium salts, 138
— on chromic acid, 171
— on cobalt salts, 117
— on copper salts, 134
— on gold salts, 143
— on indium salts, 126
— on iodates, 174
— on iridium salts, 166
— on iron protoxide salts, 119
— on iron sesquioxide salts, 121
— on lead salts, 130
— on manganese salts, 113
— on mercury oxide salts, 132
— on mercury subsalts, 129
— on molybdic acid, 167
— on molybdates, 167
— on nickel salts, 115
— on nitrites, 204
— on osmic acid, 141
— on palladium salts, 140
— on platinum salts, 144
— on rhodium salts, 140
— on ruthenium salts, 142
— on selenious acid, 169
— on silver salts, 128
— on sulphites, 173
— on tellurous acid, 168
— on thallium protoxide salts, 125
— on thallium trioxide salts, 125
— on tin binoxide salts, 148
— on tin protoxide salts, 146
— on tungstates, 168
— on uranium salts, 124
— on vanadic acid, 126
— on zinc salts, 112
Hypochlorites, properties, 205
— reactions, 205
Hypochlorous acid, properties, 205
— reactions, 205
Hyponitric acid, reaction, 205
— on bromides, 193
— on iodides, 195
Hypophosphites, properties, 205
— reactions, 205
Hypophosphorous acid, properties, 205
— reactions, 205
Hyposulphites and sulphites, detection in presence of sulphides, 174
— properties, 174
— reactions, 174

Ignition, 18
Incrustations, obtained with Bunsen lamp, 24
Indigo, preparation of solution, 73

Indigo, uses as reagent, 73
— on chlorates, 208
— on chlorates and sulphurous acid, 207
— on chlorites, 205
— on hypochlorites, 205
— on nitrates, 207
— on osmic acid, 141
— on perchloric acid, 209
Ind go prism, 27
Indium, occurrence, 125
— properties, 125
— reactions, 126
Indium carbonate, properties, 126
Indium oxide, properties, 125
Indium salts, properties, 126
Indium sulphide, properties, 126
Iodates, properties, 174
— reactions, 174
Iodic acid, properties, 174
— reactions, 174
Iodides, insoluble, decomposition, 197
— properties, 195
Iodine, detection, 202
— as reagent for alkaloids, 344
— properties, 195
— reactions, 195
— on lanthanium salt, 107
Iridium, detection in analytical course, 338, 340
— occurrence, 166
— properties, 166
— reactions, 166
Iridium and ammonium chloride, properties, 166
Iridium and potassium chloride, properties, 166
Iron, properties, 119
— reactions, 119
— uses as reagent, 53
— separation from other members of Group 4, 122
— on copper salts, 135
— on sulphides and hydrochloric acid, 201
Iron acetate, properties, 218
Iron benzoate, properties, 217
Iron ferricyanide, properties, 120
Iron ferrocyanide, properties, 121
Iron and potassium ferrocyanide, properties, 120
Iron protosesquioxide, properties, 121
Iron protoxide, detection in presence of sesquioxide, 124
— properties, 119
— reactions, 119
Iron protoxide salts, properties, 119
Iron sesquichloride, preparation, 67
— tests of purity, 67
— uses as reagent, 68
— on acetates, 218
— on benzoates, 217
— on ferricyanides, 200
— on ferrocyanides, 199
— on formates, 219
— on hyposulphites, 174
— on iodides, 197, 203
Iron sesquichloride on phosphates, 178
— on succinates, 216
Iron sesquioxide, detection in presence of protoxide, 124
— properties, 120
— reactions, 121
Iron sesquioxide salts, properties, 121
Iron succinate, properties, 216
Iron sulphate, preparation, 67
— tests of purity, 67
— uses as reagent, 67
— on chlorites, 205
— on cyanides, 198
— on ferricyanides, 200
— on gold salts, 143
— on iridium salts, 166
— on nitrates, 206
— on nitrites, 204
— on osmic acid, 141
— on palladium salts, 140
— on platinum salts, 145
— on selenious acid, 206
Iron sulphide, preparation, 44
— properties, 120
Iron sulphocyanide, properties, 121

LACTATES, properties, 221
Lactic acid, properties, 221
— reactions, 221
Lamp, Berzelius, 19
— Bunsen, 20
— improved Bunsen, 22
— three Bunsen, 22
— spirit, 19
Lanthanium, detection in anal. course, 339
— occurrence, 106
— reactions, 107
— oxide, properties, 107
— salts, properties, 107
Lead, properties, 130
— reactions, 130
— separation from Gr. 5, Div. 2, 138
— separation from silver and mercurous oxide, 131
Lead acetate, preparation of solution, 68
— tests of purity, 68
— uses as reagent, 68
— on benzoates, 217
— on chlorides, 192
— on chromates, 172
— on citrates, 212
— on hydrofluosilicic acid, 176
— on hypophosphites, 205
— on malates, 213
— on phosphites, 187
— on tartrates, 211
— on succinates, 216
— on sulphates, 175
— on sulphides, 201
— on tungstates of alkalies, 168
— on vanadates, 126
Lead binoxide on cerium salts, 106
— on chromium salts, 101

Lead binoxide on manganese salts, 114
Lead carbonate, properties, 131
Lead chloride, properties, 131
Lead chromate, properties, 172
Lead citrate, properties, 212
Lead malate, properties, 213
Lead nitrate on chloride lime, 205
Lead oxide on acetic acid, 219
— on formic acid, 220
Lead oxides, properties, 130
Lead salts, properties, 130
Lead succinate, properties, 216
Lead sulphate, properties, 131
Lead sulphide, properties, 130
Lead tartrate, properties, 210
LIEBIG'S condenser, 12
Lime, preparation of hydrate, 52
— properties, 93
— reactions, 93
— separation from other alkaline earths, 97
— uses as reagent, 53
— on ammonia salts, 85
— on magnesia salts, 95
Lime water, preparation, 52
— preparation of pure, 52
— uses as reagent, 52
— on carbonic acid, 188
— on citrates, 212
— on malates, 213
— on racemates, 215
— on tartrates, 210
Lime carbonate, properties, 93
Lime citrate, properties, 211
Lime chloride, properties, 215
Lime lactate, preparation, 221
— properties, 222
Lime malate, properties, 213
Lime oxalate, properties, 93
Lime phosphate, properties, 178
Lime racemate, properties, 215
Lime salts, properties, 93
Lime succinate, properties, 216
Lime sulphate, preparation of solution, 65
— properties, 93
— uses as reagent, 65
— on baryta salts, 90
— on oxalates, 182
— on phosphates, 178
— on racemates, 215
— on strontia salts, 92
— on tartrates, 210
Lime tartrate, properties, 210
Lithia, detection in analytical course, 340
— rubidia and cæsia, detection in presence of much potassa and soda, 89
— distribution, 88
— properties, 88
— reactions, 88
Lithia phosphate, properties, 88
Lithia salts, properties, 88
Litmus paper, blue, preparation, 71
— blue, uses as reagent, 72
— rationale of action, 72
— red, preparation, 72
Litmus paper, red, uses as reagent, 72
Logwood decoction on chromates, 173

MAGNESIA, properties, 94
— reactions, 95
— separation from other alkaline earths, 97
— on malic acid, 213
Magnesia and ammonia arsenate, properties, 162
Magnesia and ammonia phosphate, properties, 96
Magnesia carbonate, properties, 95
Magnesia malate, properties, 213
Magnesia oxalate, properties, 96
Magnesia phosphate, properties, 96
Magnesia pyrophosphate, properties, 180
Magnesia salts, properties, 95
Magnesia sulphate, preparation of solution, 66
— purification, 66
— tests of purity, 66
— uses as reagent, 66
— on phosphates, 178
— on pyrophosphates, 180
Magnesia sulphate, ammonium chloride and ammonia, on arsenates, 162
— on metaphosphates, 180
— on phosphates, 178
— on phosphites, 187
Magnesium, properties, 94
— on phosphates, 180
Malates, properties, 213
— reactions, 213
Malic acid, detection, 214
— properties, 212
— reactions, 213
Manganese, properties, 113
— reactions, 113
— separation from other members of Gr. 4., 122
Manganese binoxide on bromides, 194
— on chlorides, 192
— on iodides, 196
— on oxalates, 183
Manganese ferricyanide, properties, 114
Manganese ferrocyanide, properties, 114
Manganese oxides, properties, 113
Manganese salts, properties, 113
— on chloride lime, 205
Manganese sulphide, properties, 113
MARSH'S test for arsenic, 156
Mercury, properties, 128
— reactions, 129
Mercury chloride, preparation of solution, 69
— uses as reagent, 69
— on acetates, 219
— on formates, 220
— on hypophosphites, 205
— on phosphites, 187
— on sulphites, 173
— on tin protoxide salts, 133, 146
Mercury cyanide on palladium salts, 140
Mercury oxide, properties, 132

Mercury oxide, reactions, 132
— separation from other members of Group 5, Div. 2, 138
Mercury oxide salts, properties, 132
Mercury and potassium iodide as reagent for alkaloids, 344
Mercury subacetate, properties, 219
Mercury subchloride, properties, 129
Mercury subformate, properties, 220
Mercury subnitrate, preparation, 69
— tests of purity, 69
— uses as reagent, 69
— on acetates, 219
— on chlorides, 192
— on formates, 220
— on phosphites, 187
— on tungstates, 168
— on vanadates, 126
Mercury suboxide, properties, 128
— reactions, 129
— separation from silver and lead, 131
Mercury subsalts, properties, 129
Mercury sulphide, properties, 132
Metallic oxides, groups, 81
Metaphosphates, properties, 180
— reactions, 180
Metaphosphoric acid, reactions, 180
Metastannic acid, properties, 147
Metastannic chloride, properties, 147
Metatungstic acid as reagent for alkaloids, 345
Microcosmic bead, testing with, 79
— with cerium salts, 106
— with chromium salts, 102
— with cobalt salts, 119
— with didymium oxide, 107
— with erbium oxide, 106
— with iron salts, 120
— with manganese salts, 115
— with nickel salts, 116
— with niobic acid, 110
— with silicates, 190
— with tantalic acid, 110
— with titanic acid, 109
— with tungstic acid, 168
— with uranium salts, 124
— with yttria, 105
— and copper oxide with bromides, 194
— and copper oxide with chlorides, 192
— and copper oxide with iodides, 197
Microcosmic salt, as blowpipe test for fluorine, 185
— effects of heat on, 79
— preparation, 78
— tests of purity, 78
— uses as flux, 79
Mineral water analysis, 292
Molybdenum, detection in analytical course, 338, 340
— occurrence, 166
— properties, 166
— reactions, 167
Molybdenum oxides, properties, 166
Molybdenum sulphide, properties, 167
Molybdic acid, properties, 167
Morphine, detection, 364, 366, 369
— properties, 349
— reactions, 349
Morphine salts, properties, 349

NARCOTINE, detection, 355, 364, 366, 369
— properties, 351
— reactions, 351
Narcotine salts, properties, 351
NESSLER'S solution, preparation, *footnote*, 87
Nickel, properties, 115
— reactions, 115
— separation from other members of Gr. 4, 122
Nickel ferricyanide, properties, 116
Nickel ferrocyanide, properties, 116
Nickel oxide, properties, 115
Nickel and potassium cyanide, properties, 116
Nickel salts, properties, 115
Nickel sesquioxide, properties, 115
Nickel sulphide, properties, 115
Nicotine, detection, 348
— properties, 346
— reactions, 346
Nicotine salts, properties, 346
Niobic acid, detection in analytical course, 336, 339, 340
— occurrence, 110
— properties, 110
— reactions, 110
Niobium oxyfluoride and potassium fluoride, properties, 110
Nitrates, properties, 206
— reactions, 206
Nitric acid, detection, 208
— detection of free, 208
— properties, 206
— purification, 39
— reactions, 206
— tests of purity, 39
— uses as reagent, 39
— on bromides, 193
— on iodides, 195
— on perchlorates, 209
— on thallium protoxide salts, 125
Nitrites, properties, 204
— reactions, 204
Nitrohydrochloric acid, nature, 42
— preparation, 42
— uses as reagent, 43
Nitrous acid, properties, 204
— reactions, 204
— on iodides, 195

OSMIC acid, properties, 141
Osmium, detection in analytical course, 338, 340
— occurrence, 141
— properties, 141
— reactions, 141
Osmium oxides, properties, 141

Osmium salts, properties, 141
Oxalates, properties, 182
— reactions, 182
Oxalic acid, detection, 186, 214
— properties, 182
— purification, 56
— reactions, 182
— on alumina salts, 100
— on berylla salts, 103
— on cerium salts, 106
— on didymium salts, 107
— on iridium salts, 166
— on lanthanium salts, 107
— on thoria salts, 104
— on yttria salts, 105
— on zirconia salts, 104
Oxidizing flame, 17

PALLADIUM, detection in analytical course, 338
— occurrence, 139
— properties, 139
— reactions, 140
Palladium and ammonium chloride, properties, 140
Palladium-ammonium chloride, properties, 140
Palladium chloride on bromides, 193
— on iodides, 195
Palladium cyanide, properties, 140
Palladium iodide, properties, 195
Palladium nitrate on bromides, 193
— on iodides, 195
Palladium oxides, properties, 140
Palladium and potassium chloride, properties, 140
Palladium salts, properties, 140
Palladium and sodium chloride, preparation, 71
— uses as reagent, 71
Palladium sulphide, properties, 140
Perchlorates, properties, 209
— reactions, 209
Perchloric acid, properties, 209
— reactions, 209
Phosphates, insoluble, decomposition, 179
— properties, 177
— reactions, 177
Phosphoantimonic acid, as reagent for alkaloids, 345
— preparation, *footnote*, 345
Phosphomolybdic acid, as reagent for alkaloids, 345
— preparation, *footnote*, 345
Phosphoric acid, detection, 186
— properties, 177
— reactions, 177
— separation from alkaline earths, 178
Phosphorous acid, properties, 187
— reactions, 187
Phosphorus, detection in poisoning cases, 318
— properties, 176
Picric acid, as reagent for alkaloids, 345
Picric acid on cyanides, 198
Picrotoxine, detection, 364, 366, 369
— properties, 363
— reactions, 363
Platinum, crucibles, size, 31
— crucibles, rules for using, 14
— properties, 144
— reactions, 144
— separation from gold, 145
— triangle, 20
— wire, 18
Platinum and ammonium chloride, properties, 85, 144
Platinum chloride, as reagent for alkaloids, 344
— preparation, 70
— tests of purity, 70
— uses as reagent, 70
— on ammonia salts, 85
— on cæsia salts, 87
— on lithia salts, 88
— on potassa salts, 82
— on potassium iodide, 86
— on rubidia salts, 87
— on soda salts, 85
— on thallium protoxide salts, 125
Platinum oxides, properties, 144
Platinum and potassium chloride, properties, 82, 144
— solubility, 87
Platinum salts, properties, 144
Platinum sulphide, properties, 144
Poisons, detection of inorganic, 306
— detection of organic, 364
Potable water analysis, 289
Potassa, preparation by baryta, 50
— properties, 82
— purification by alcohol, 49
— reactions, 82
— separation from other alkalies, 86
— tests of purity, 50
— uses as reagent, 50
— on alumina salts, 99
— on ammonia salts, 85
— on antimony salts, 150
— on baryta salts, 90
— on berylla salts, 103
— on bismuth salts, 136
— on bromine, 194
— on cadmium salts, 138
— on cerium salts, 106
— on chromium salts, 101
— on cobalt salts, 117
— on copper salts, 134
— on didymium salts, 107
— on indium salts, 126
— on iridium salts, 166
— on iron protoxide salts, 120
— on iron sesquioxide salts, 121
— on lanthanium salts, 107
— on lead salts, 130
— on lime salts, 93
— on magnesia salts, 95
— on manganese salts, 114
— on mercury oxide salts, 133

Potassa on mercury salts, 129
on nickel salts, 115
on osmic acid, 141
on palladium salts, 140
on rhodium salts 140
on ruthenium salts, 142
on silver salts, 128
on strontia salts, 91
on tellurous acid, 169
on thallium peroxide salts, 125
on thallium trioxide salts, 125
on thoria salts, 103
on tin binoxide salts, 148
on tin peroxide salts, 146
on titanic acid, 108
on uranium salts, 124
on yttria salts, 105
on zinc salts, 112
on zirconia salts, 104
fusion with niobic acid, 110
fusion with tantalic acid, 109
fusion with titanic acid, 109
Potassa acid sulphate, see *Potassa bisulphate*
Potassa alum, solubility, 88
Potassa antimonate, preparation, 66
preparation of solution, 60
tests of purity, 60
uses as reagent, 60
on soda salts, 34
Potassa bicarbonate on niobate of potassa, 110
on uranium salts, 124
Potassa bichromate, preparation of solution, 60
purification, 60
uses as reagent, 60
on baryta salts, 91
on bismuth salts, 136
on lime salts, 94
on strontia salts, 92
Potassa bisulphate, preparation, 76
tests of purity, 76
uses as flux, 76
with niobic acid, 110
with tantalic acid, 109
with titanic acid, 108
with tungstic acid, 167
and calcium fluoride on borates, 181
Potassa bitartrate, properties, 82
solubility, 88
Potassa carbonate. See *Soda carbonate.*
Potassa chlorate and soda carbonate as blowpipe test for chromium, 102
Potassa chromate on baryta salts, 91
on bromides, 194
on chlorides, 192
on indium salts, 126
on iodides, 129
on lead salts, 131
— on lime salts, 94
— on magnesia salts, 96
— on strontia salts, 92
Potassa nitrite, preparation, 59
preparation of solution, 59
Potassa nitrite, tests of purity, 59
— uses as reagent, 59
— on bromides, 193
— on cobalt salts, 118
— on gold salts, 144
— on iridium salts, 166
— on iodides, 196
— on nickel salts, 116
— on palladium salts, 140
— on rhodium salts, 140
— on ruthenium salts, 142
— on osmic acid, 141
Potassa permanganate on chloride of lime, 205
— on chlorites, 205
— on sulphites, 173
Potassa percyanate, formation, 198
Potassa salts, properties, 32
— on hydrofluosilicic acid, 176
— on perchloric acid, 209
— on racemates, 215
— on tartrates, 210
Potassa and soda carbonate, preparation, 73
— tests of purity, 73
— uses as flux, 74
— fusion with insoluble bromides, 194
— fusion with insoluble chlorides, 192
— fusion with insoluble iodides, 197
— fusion with insoluble silicates, 196
— fusion with insoluble sulphates, 175
Potassa sulphate, preparation of solution, 56
— purification, 56
— uses as reagent, 56
— on alumina salts, 100
— on cerium salts, 106
— on didymium salts, 107
— on lanthanium salts, 107
— on lime salts, 93
— on thoria salts, 104
— on zirconia salts, 104
Potassa tantalate, properties, 110
Potassium acid fluoride with beryllia salts, 103
— with titanic acid, 108
Potassium chloride on iridium salts, 166
— on palladium salts, 140
— on platinum salts, 144
— on ruthenium salts, 141
Potassium cobalticyanide, formation, 118
Potassium cyanide, preparation, 62
— preparation of solution, 62
— tests of purity, 62
— uses as reagent, 62
— uses as dry reducing agent, 77
— on chlorates, 207
— on cobalt salts, 118
— on nickel salts, 116
— on nitrates, 206
— on tellurium compounds, 168
— on selenium compounds, 169
— and cobalt solution on nitrites, 204
— and soda carbonate as dry reducing agent, 77

Potassium cyanide and soda carbonate as test for antimony, 152
— and soda carbonate as test for arsenic, 158
— and soda carbonate as test for tin, 147
Potassium ferricyanide, preparation, 63
— preparation of solution, 63
— tests of purity, 63
— uses as reagent, 63
— on cobalt salts, 118
— on indium salts, 126
— on iron protoxide salts, 120
— on iron sesquioxide salts, 121
— on manganese salts, 114
— on nickel salts, 116
— on zinc salts, 112
— and tartaric acid on cobalt salts, 118
Potassium ferrocyanide, preparation of solution, 63
— uses as reagent, 63
— on cobalt salts, 118
— on copper salts, 135
— on indium salts, 126
— on manganese salts, 114
— on molybdates, 167
— on nickel salts, 116
— on iron protoxide salts, 120
— on iron sesquioxide salts, 121
— on tantalic acid, 110
— on titanic acid, 108
— on tungstates, 168
— on uranium salts, 124
— on vanadic acid, 126
— on vanadates, 127
— on zinc salts, 112
Potassium fluoride on niobic acid, 110
Potassium iodide on antimonic acid, 149
— on osmic acid, 141
— on palladium salts, 140
— on thallium protoxide salts, 125
— on thallium trioxide salts, 125
Potassium and platinum chloride, properties, 82
— solubility, 87
Potassium sulphocarbonate, preparation, *footnote*, 116
— on cobalt salts, 118
— on nickel salts, 116
Potassium sulphocyanide, preparation, 63
— preparation of solution, 64
— tests of purity, 64
— uses as reagent, 64
— on hyponitric acid, 204
— on indium salts, 126
— on iron protoxide salts, 120
— on iron sesquioxide salts, 121
— on nitrites, 204
— on ruthenium salts, 142
— and sulphurous acid on cadmium salts, 138
— and sulphurous acid on copper salts, 135
— and sulphurous acid on palladium salts, 140
Potassium sulphocyanide and zinc on molybdic acid, 167
Precipitation, 6
Preliminary examination, 225
Propionic acid, detection, 221
— properties, 221
— reactions, 221
Prussian blue, properties, 121
Purple of Cassius, 143
Pyrogallic acid on nitrites, 204
Pyrophosphoric acid, properties, 180
— reactions, 180

QUININE, detection, 355, 364, 366
— properties, 353
— reactions, 353
Quinine salts, properties, 353

RACEMATES, properties, 215
— reactions, 215
Racemic acid, properties, 215
— reactions, 215
Reducing agent, dry, 77
Reducing flame, 17
REINSCH'S test for arsenic, 155
Rhodium, detection in analytical course, 338, 340
— occurrence, 140
— properties, 140
— reactions, 140
Rhodium oxides, properties, 140
Rubidia, detection in analytical course, 340
— cæsia and lithia, detection in presence of much potassa or soda, 89
— and cæsia, differences from potassa, 87
— distribution, 87
— reactions, 87
Rubidia alum, solubility, 88
Rubidia bitartrate, solubility, 88
Rubidia carbonate, solubility in alcohol, 88
Rubidium and platinum chloride, solubility, 87
Ruthenium, detection in analytical course, 338, 340
— occurrence, 141
— properties, 141
— reactions, 141

SALICINE, detection, 364, 366
— properties, 362
— reactions, 362
Selenetted hydrogen, formation, 169
Selenic acid, properties, 169
Selenious acid, properties, 169
Selenites, properties, 169
Selenium, detection in analytical course, 338
— occurrence, 169
— properties, 169
— reactions, 169
Silicates, analysis, 283
— insoluble, decomposition, 189

Silicates, properties, 189
Silicic acid, detection, 191
— properties, 189
— reactions, 189
Silicofluorides, properties, 176
Silver, properties, 127
— reactions, 128
— separation from lead and mercury suboxide, 131
Silver acetate, properties, 218
Silver arsenate, properties, 162
Silver arsenite, properties, 155
Silver borate, properties, 181
Silver bromide, properties, 193
Silver chloride, properties, 128
Silver chromate, properties, 172
Silver citrate, properties, 212
Silver cyanide, properties, 198
Silver ferricyanide, properties, 200
Silver ferrocyanide, properties, 199
Silver formate, properties, 219
Silver hyposulphite, properties, 174
Silver iodate, properties, 174
Silver iodide, properties, 195
Silver malate, properties, 213
Silver nitrate, preparation of solution, 68
— tests of purity, 68
— uses, 68
— on acetates, 218
— on antimony teroxide, 151
— on arsenates, 162
— on arsenites, 155
— on borates, 181
— on bromides, 193
— on chlorides, 192
— on chloride lime, 205
— on chlorites, 205
— on chromates, 172
— on citrates, 212
— on cyanides, 198
— on ferricyanides, 200
— on ferrocyanides, 199
— on formates, 219
— on hypophosphites, 205
— on hyposulphites, 174
— on iodates, 174
— on iodides, 195
— on malates, 213
— on metaphosphates, 180
— on nitrites, 204
— on oxalates, 182
— on perchlorates, 209
— on phosphates, 178
— on phosphites, 187
— on pyrophosphates, 180
— on sulphides, 201
— on tartrates, 210, 211
— on tungstates, 168
— on vanadates, 126
Silver oxalate, properties, 182
Silver oxide, properties, 128
Silver phosphate, properties, 178
Silver pyrophosphate, properties, 180
Silver salts, properties, 128
Silver sulphide, properties, 128
Silver tartrate, properties, 211
Soda, filtration of solution, 49
— preparation of solution, 49
— preservation of solution, 49
— properties, 83
— reactions, 84
— separation from other alkalies, 86
— tests of purity, 49
— uses as reagent, 50
— on niobate of potassa, 110
— on tantalate of soda, 110
— see *Potassa*
— fusion with niobic acid, 110
— fusion with tantalic acid, 110
Soda acetate, preparation, 57
— preparation of solution, 57
— tests of purity, 57
— uses as reagent, 57
— on indium salts, 126
Soda and ammonia phosphate, see *Microcosmic salt*
— bead, see *Microcosmic bead*
Soda antimonate, properties, 84
Soda biborate, see *Borax*
— bead, see *Borax bead*
Soda bicarbonate on uranium salts, 124
Soda bisulphite, preparation, 59
— tests of purity, 59
— uses as reagent, 59
Soda bitartrate, preparation, 40
— preparation of solution, 40
— uses as reagent, 40
— on ammonia salts, 85
— on potassa salts, 82
— on soda salts, 85
Soda carbonate, preparation of solution, 57
— purification, 57
— tests of purity, 58
— uses as reagent, 58
— uses as flux, 76
— on alumina salts, 100
— on antimony salts, 150
— on baryta salts, 90
— on berylla salts, 103
— on bismuth salts, 136
— on cadmium salts, 138
— on cerium salts, 106
— on chromium salts, 101
— on copper salts, 134
— on didymium salts, 107
— on indium salts, 126
— on lead salts, 130
— on lime salts, 93
— on magnesia salts, 95
— on strontia salts, 91
— on tellurous acid, 168
— on thallium protoxide salts, 125
— on thoria salts, 103
— on tin binoxide salts, 148
— on tin protoxide salts, 146
— on yttria salts, 105
— on zinc salts, 112
— on zirconia salts, 104
— fusion with mercury salts, 129
— fusion with niobic acid, 110

Soda carbonate, fusion with titanic acid, 109
— see *Potassa and soda carbonate*
Soda carbonate bead, with didymium salts, 107
— with iridium salts, 166
— with manganese salts, 114
— with palladium salts, 140
— with rhodium salts, 140
— with silicates, 190
Soda carbonate on charcoal as blowpipe test, 76
— for arsenic, 161
— for bismuth, 137
— for cadmium, 138
— for copper, 135
— for lead, 131
— for silver, 128
— for sulphates, 175
— for tungsten, 168
— for zinc, 113
Soda carbonate and potassium cyanide, as dry reducing agent, 77
— as test for antimony, 152
— as test for arsenic, 158
— as test for tin, 147
Soda hyposulphite or cerium protoxide salts, 106
— on nitrate of sesquioxide of cerium, 106
— on didymium salts, 107
— on thoria salts, 104
— on titanic acid, 108
— on yttria salts, 105
— on zirconia salts, 104
— as blowpipe test for cyanogen, 198
Soda nitrate, preparation, 75
— tests of purity, 75
— uses as dry reagent, 75
— and soda carbonate as test for chromium, 102
Soda phosphate, preparation of solution, 56
— purification, 56
— tests of purity, 56
— uses as reagent, 56
— on alumina salts, 100
— on baryta salts, 90
— on indium salts, 126
— on lime salts, 93
— on lithia salts, 88
— on magnesia salts, 96
— on strontia salts, 91
— on titanic acid, 108
— ammonium chloride and ammonia on magnesia salts, 96
Soda and potassa carbonate, see *Potassa and soda carbonate.*
Soda salts, properties, 84
Soda sulphate on lime salts, 93
— on tin binoxide salts, 148
Soda sulphite on osmic acid, 141
— on tellurous acid, 168
Soda tantalate, properties, 110
Sodium on phosphates, 180
Sodium nitroprusside on sulphides, 201
Sodium and platinum chloride, properties, 85
Sodium sulphide, preparation, 55
— preparation of yellow, 55
— uses as reagent, 55
Soils analysis, 300
Solubility table, 380
Solution, 3, 233
Solvents, chemical, 3
— simple, 3
Spectroscope, 28
— KIRCHHOFF and BUNSEN'S, 28
— REXROTH'S, 29
Spectrum of baryta salts, 91
— of borates, 182
— of cæsia salts, 88
— of copper bromide, 204
— of copper chloride, 204
— of copper iodide, 204
— of didymium salts, 107
— of erbium salts, 105
— of indium salts, 126
— of lime salts, 94
— of lithia salts, 88
— of potassa salts, 83
— of rubidia salts, 88
— of soda salts, 84
— of strontia salts, 93
— of thallium salts, 125
— absorption, of didymium salts, 107
— absorption, of erbium salts, 105
Spirit lamps, 19
Starch on bromine, 194
— on iodine, 196, 203
— and potassium iodide on nitrites, 204
Starch bromide, properties, 194
Starch iodide, properties, 196, 203
— on cyanides, 199
— on hyposulphites, 174
— on sulphites, 173
Strontia, and baryta, detection of minute quantities in presence of lime, 98
— properties, 91
— reactions, 92
— separation from other alkaline earths, 97
Strontia chromate, properties, 92
Strontia oxalate, properties, 92
Strontia salts, properties, 91
Strontia sulphate, properties, 92
Strontium chloride on hydrofluosilicic acid, 176
Strychnine, detection, 361, 364, 366, 369, 372, 373
— properties, 356
— reactions, 356
Strychnine salts, properties, 356
Sublimate, definition, 13
Sublimation, 13
Succinates, properties, 216
— reactions, 216
Succinic acid, detection, 217
— properties, 215
— reactions, 216
Sulphates, decomposition of insoluble, 175

Sulphates, properties, 175
— reactions, 175
Sulphides, properties, 200
— reactions, 201
Sulphites, and hyposulphites, detection in presence of sulphides, 174
— properties, 173
— reactions, 173
Sulphur, detection, 202
— detection in thallium, 125
— properties, 200
Sulphuretted hydrogen, see *Hydrosulphuric acid*
Sulphuric acid, detection, 175
— detection of free, 176
— preparation of solution, 38
— properties, 174
— purification, 37
— reactions, 175
— tests of purity, 38
— uses as reagent, 38
— on baryta salts, 90
— on bismuth salts, 136
— on lead salts, 131
— on lime salts, 93
— on magnesia salts, 96
— on strontia salts, 92
— on tantalates, 109
Sulphuric acid concentrated, on acetates, 219
— on chlorates, 208
— on citrates, 212
— on ferricyanides, 200
— on ferrocyanides, 199
— on fluorides, 184
— on formates, 220
— on iodides, 196
— on malates, 213
— on niobic acid, 110
— on oxalates, 183
— on perchloric acid, 209
— on silicofluorides, 176
— on tartrates, 211
— and silica on fluorides, 185
Sulphurous acid, properties, 173
— reactions, 173
— on arsenates, 161
— on chromates, 172
— on iridium binoxide, 166
— on iodates, 174
— on perchlorates, 209
— on selenious acid, 169
— on vanadic acid, 126

TANNIC acid on gold salts, 144
Tantalic acid, detection in analytical course, 339, 340
— occurrence, 109
— properties, 109
— reactions, 109
Tantalum chloride, properties, 109
Tantalum and potassium fluoride, properties, 109
Tartaric acid, detection, 214
Tartaric acid, preparation of solution, 40
— properties, 209
— reactions, 210
— uses as reagent, 40
— on ammonia salts, 85
— on cæsia salts, 87
— on lithia salts, 88
— on potassa salts, 82
— on rubidia salts, 87
— on soda salts, 85
Tartrates, properties, 209
— reactions, 210
Telluretted hydrogen, formation, 168
Telluric acid, properties, 168
Tellurium, detection in analytical course, 338
— occurrence, 168
— properties, 168
— reactions, 168
Tellurium oxides, properties, 168
Tellurous acid, properties, 168
Terbium, *footnote*, 105
Thallium, detection in analytical course, 336, 338, 339
— detection in sulphur, 125
— distribution, 124
— properties, 124
— reactions, 125
Thallium oxides, properties, 125
Thallium and platinum chloride, properties, 125
Thallium protiodide, properties, 125
Thallium protocarbonate, properties, 125
Thallium protochloride, properties, 125
Thallium protoxide salts, reactions, 125
Thallium salts, properties, 125
Thallium sulphide, properties, 125
Thallium trioxide salts, reactions, 125
Thoria, detection in analytical course, 339, 340
— occurrence, 103
— properties, 103
— reactions, 103
Thoria carbonate, properties, 103
Thoria oxalate, properties, 104
Thoria and potassa sulphate, properties, 104
Thoria salts, properties, 102
Thoria sulphate, properties, 104
Thorium fluoride, properties, 103
Tin, properties, 145
— separation from antimony and arsenic, 163
— on niobic acid, 110
— on titanic acid, 108
Tin binoxide, properties, 147
— salts, properties, 147
— salts, reactions, 148
— separation from tin protoxide, 165
Tin bisulphide, properties, 148
Tin protochloride, preparation, 70
— preservation, 70
— properties, 146
— tests of purity, 70

Tin protochloride, uses as reagent, 70
— on bismuth salts, 137
— on gold salts, 143
— on iridium salts, 166
— on mercury oxide salts, 133
— on mercury subsalts, 129
— on osmic acid, 141
— on palladium salts, 140
— on platinum salts, 145
— on selenious acid, 169
— on sulphurous acid, 173
— on tellurous acid, 168
— on tungstates, 168
Tin protosulphide, properties, 146
Tin protoxide, properties, 146
— reactions, 146
— separation from tin binoxide, 165
— salts, properties, 146
Titanic acid, detection in analytical course, 339, 340
— distribution, 108
— properties, 108
— reactions, 107
Titanium chloride, properties, 108, 109
Titanium and potassium fluoride, properties, 108
Triangle, platinum, 20
Tungstates, insoluble, decomposition, 168
Tungsten, detection in analytical course, 336, 340
— occurrence, 167
— properties, 167
— reactions, 167
Tungsten oxides, properties, 167
Tungstic acid, properties, 167
Turmeric paper, preparation, 72
— uses as reagent, 73
— with ammonia molybdate, 181
— with boracic acid, 181
— with hydrochloric acid, 181
— with iron sesquichloride, 181
— with zirconia, 181

URANIUM, detection in analytical course, 339
— occurrence, 124
— reactions, 124
Uranium oxides, properties, 124
Uranium oxysulphide, properties, 124

VANADATES, properties, 126
Vanadic acid, detection in analytical course, 340
— occurrence, 126
— properties, 126
— reactions, 126
Vanadium oxides, properties, 126
Vanadium pentasulphide, properties, 126
Veratrine, detection, 361, 364, 366, 369
— properties, 359
— reactions, 359
— salts, properties, 359

WASHING, 9
Washing bottle, 9
Water, analysis of mineral, 292
— analysis of potable, 289
— bath, 12
— distillation, 35
— tests of purity, 35
— uses as reagent, 35
— on antimony salts, 149
— on bismuth salts, 137

YTTRIA, detection in analytical course, 339
— occurrence, 104
— properties, 104
— reactions, 105
— separation from erbia, 106
Yttria carbonate, properties, 105
Yttria and potassa sulphate, properties, 105
Yttria salts, properties, 105
Yttria sulphate, properties, 105

ZINC, preparation of granulated, 53
— properties, 111
— purification from arsenic, 53
— reactions, 112
— separation from other members of Gr. 4, 122
— tests of purity, 53
— uses as reagent, 53
— on antimony salts, 151
— on arsenic compounds, 156
— on chromates, 172
— on copper salts, 135
— on hypophosphites, 205
— on hyposulphites, 174
— on indium salts, 126
— on iridium salts, 166
— on molybdates, 167
— on niobic acid, 110
— on nitrates, 207
— on osmic acid, 141
— on phosphorous acid, 187
— on rhodium salts, 140
— on ruthenium salts, 142
— on sulphites, 173
— on tantalic acid, 109
— on tellurous acid, 168
— on thallium protoxide salts, 125
— on tin salts, 147, 148
— on titanic acid, 108
— on tungstates, 168
— on vanadic acid, 126
Zinc and platinum on antimony salts, 150
Zinc, basic carbonate, properties, 112
Zinc ferricyanide, properties, 113
Zinc ferrocyanide, properties, 112
Zinc oxide, properties, 111
Zinc salts, properties, 111
Zinc sulphate and sodium nitroprusside on sulphites, 173
Zinc sulphide, properties, 112

Zircon, decomposition, 104
Zirconia, detection in analytical course, 339, 340
— occurrence, 104
— properties, 104
— reactions, 104
Zirconia carbonate, properties, 104
Zirconia hyposulphite, properties, 104
Zirconia oxalate, properties, 104
Zirconia and potassa sulphate, properties, 104
Zirconia salts, properties, 104
Zirconia silicates, decomposition, 104
Zirconia sulphate, properties, 104

THE END.

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# A CLASSIFIED INDEX

TO

# MESSRS. J. & A. CHURCHILL'S CATALOGUE.

## ANATOMY.


| | PAGE |
|---|---|
| Anatomical Remembrancer | 7 |
| Flower on Nerves | 16 |
| Heale's Anatomy of the Lungs | 19 |
| Heath's Practical Anatomy | 20 |
| Holden's Human Osteology | 20 |
| Do. on Dissections | 20 |
| Jones' and Sieveking's Patho-logical Anatomy | 22 |
| Maclise's Surgical Anatomy | 25 |
| Sibson's Medical Anatomy | 33 |
| Waters' Anatomy of Lung | 38 |
| Wilson's Anatomy | 39 |


## CHEMISTRY.


| | |
|---|---|
| Bernays' Notes for Students | 9 |
| Bloxam's Chemistry | 10 |
| Do. Laboratory Teaching | 10 |
| Bowman's Practical Chemistry | 10 |
| Do. Medical do. | 10 |
| Brown's Analytical Tables | 11 |
| Fownes' Manual of Chemistry | 16 |
| Do. Actonian Prize | 16 |
| Do. Qualitative Analysis | 16 |
| Fresenius' Chemical Analysis | 17 |
| Galloway's First Step | 17 |
| Do. Second Step | 17 |
| Do. Analysis | 17 |
| Do. Tables | 17 |
| Griffiths' Four Seasons | 18 |
| Horsley's Chem. Philosophy | 21 |
| Kay-Shuttleworth's Modern Chemistry | 23 |
| Mulder on the Chemistry of Wine | 27 |
| Speer's Pathol. Chemistry | 34 |
| Sutton's Volumetric Analysis | 34 |
| Valentin's Laboratory Text-Book | 37 |


## CLIMATE and BATHS.


| | |
|---|---|
| Bennet's Winter in the South of Europe | 9 |
| Chambers on Italy | 12 |
| Cutler on Spa | 14 |
| Dalrymple on Egypt | 14 |
| Francis on Change of Climate | 16 |
| Grabham on Madeira | 18 |
| Hall on Torquay | 19 |
| Haviland on Climate | 19 |
| Horton on West Coast of Africa | 21 |
| Kennion on Harrogate | 23 |
| Martin on Tropical Climates | 26 |
| Moore's Diseases of India | 26 |
| Patterson's Egypt and the Nile | 28 |
| Scoresby-Jackson's Climatology | 32 |
| Shapter on South Devon | 32 |
| Siordet on Mentone | 33 |
| Taylor on Pau and Pyrenees | 35 |


## DEFORMITIES, &c.


| | PAGE |
|---|---|
| Adams on Spinal Curvature | 6 |
| Do. on Clubfoot | 6 |
| Bigg's Orthopraxy | 9 |
| Bishop on Deformities | 10 |
| Do. Articulate Sounds | 10 |
| Brodhurst on Deformities | 11 |
| Do. on Clubfoot | 11 |
| Do. on Spine | 11 |
| Coles on Deformities of the Mouth | 13 |
| Hugman on Hip Joint | 21 |


## GENERATIVE ORGANS, Diseases of, and SYPHILIS.


| | |
|---|---|
| Acton on Reproductive Organs | 6 |
| Coulson on Syphilis | 14 |
| Gant on Bladder | 17 |
| Hutchinson on Inherited Syphilis | 22 |
| Oppert on Syphilis | 27 |
| Parker on Syphilis | 28 |
| Wilson on Syphilis | 39 |


## HYGIENE.


| | |
|---|---|
| Armstrong on Naval Hygiene | 7 |
| Chavasse's Advice to a Mother | 13 |
| Do. Counsel to do. | 13 |
| Do. Advice to a Wife | 13 |
| Dobell's Germs and Vestiges of Disease | 15 |
| Godfrey on Hair | 18 |
| Gordon on Army Hygiene | 18 |
| Hartwig on Sea Bathing | 19 |
| Hartwig on Physical Education | 19 |
| Hufeland's Art of prolonging Life | 21 |
| Hunter on Body and Mind | 21 |
| Lowndes on the Maintenance of Health | 25 |
| Moore's Health in Tropics | 26 |
| Parkes on Hygiene | 28 |
| Pickford on Hygiene | 29 |
| Robertson on Diet | 31 |
| Routh on Infant Feeding | 31 |
| Turner's Manual of Diet | 36 |
| Wells' Seamen's Medicine Chest | 38 |
| Wilson on Healthy Skin | 39 |
| Do. on Mineral Waters | 39 |
| Do. on Turkish Bath | 39 |


## MATERIA MEDICA and PHARMACY.


| | |
|---|---|
| Beasley's Formulary | 9 |
| Do. Receipt Book | 9 |
| Do. Book of Prescriptions | 9 |
| Birch on Oxygen | 9 |


## MATERIA MEDICA and PHARMACY—*continued.*


| | PAGE |
|---|---|
| Brunton on Digitalis | 11 |
| Lescher's Elements of Pharmacy | 24 |
| Nevins' Analysis of Pharmacop. | 27 |
| Pereira's Selecta è Prescriptis | 28 |
| Prescriber's Pharmacopœia | 29 |
| Rogers on Therapeutics | 31 |
| Royle's Materia Medica | 31 |
| Smith's Pharmaceutical Guide | 33 |
| Squire's Hospital Pharmacopœias | 34 |
| Do. Companion to the Pharmacopœia | 34 |
| Steggall's First Lines for Chemists and Druggists | 34 |
| Stowe's Toxicological Chart | 34 |
| Taylor on Poisons | 36 |
| Waldtuch's Materia Medica | 37 |
| Waring's Therapeutics | 37 |
| Wittstein's Pharmacy | 38 |


## MEDICINE.


| | |
|---|---|
| Adams on Rheumatic Gout | 6 |
| Addison on Cell Therapeutics | 6 |
| Do. on Healthy and Diseased Structure | 6 |
| Aldis's Hospital Practice | 6 |
| Anderson on Leprosy | 7 |
| Barclay on Medical Diagnosis | 7 |
| Do. on Gout | 7 |
| Barlow's Practice of Medicine | 8 |
| Basham on Dropsy | 8 |
| Bennett on Cancerous Growths | 9 |
| Birch on Constipation | 9 |
| Braidwood on Pyæmia | 10 |
| Brinton on Stomach | 11 |
| Do. on Intestinal Obstruction | 11 |
| Budd on the Liver | 12 |
| Budd on Stomach | 11 |
| Camplin on Diabetes | 12 |
| Chambers on the Indigestions | 12 |
| Do. Lectures | 12 |
| Cobbold on Worms | 13 |
| Dale's Practical Medicine | 14 |
| Davey's Ganglionic Nervous Syst. | 14 |
| Day's Clinical Histories | 15 |
| Elam on Medicine, Disease, and Death | 15 |
| Eyre on Stomach | 15 |
| Fenwick on the Stomach | 16 |
| Do. on Diagnosis | 16 |
| Foster's Method and Medicine | 16 |
| Fuller on Rheumatism | 16 |
| Gibb on Laryngoscope | 17 |
| Habershon on the Abdomen | 18 |
| Do. on Mercury | 18 |
| Do. on the Liver | 18 |
| Headland—Action of Medicines | 19 |
| Do. Medical Handbook | 19 |
| Hood on Gout and Rheumatism | 21 |
| Hooper's Physician's Vade-Mecum | 18 |
| Inman's New Theory | 23 |

## MEDICINE—*continued.*

PAGE
James on Laryngoscope .. .. 22
Jones (Bence) on Pathology and Therapeutics .. .. .. .. 22
Leared on Imperfect Digestion . 24
Mackenzie on Throat Diseases . 25
MacLeod on Acholic Diseases .. 25
Macleod's Ben Rhydding .. .. 25
Macnamara on Cholera .. .. 25
Marcet on Chronic Alcoholism . 25
Macpherson on Cholera .. .. 26
Martyn on Hooping Cough .. 26
Meryon on Paralysis .. .. 26
Morris on Germinal Matter .. 27
Mushet on Apoplexy .. .. .. 27
Parkin on Cholera .. .. .. 28
Pavy on Diabetes .. .. .. 28
Do. on Digestion .. .. .. 28
Reynolds' Uses of Electricity .. 30
Richardson's Discourses .. .. 30
Roberts on Palsy .. .. .. 31
Robertson on Gout .. .. .. 31
Savory's Domestic Medicine .. 32
Semple on Cough .. .. .. 32
Shaw's Medical Remembrancer 32
Smee on Debility .. .. .. 33
Squire on Temperatures .. .. 34
Steggall's Medical Manual .. 34
Thomas' Practice of Physic .. 35
Thudichum on Gall Stones .. 35
Todd's Clinical Lectures .. .. 36
Turnbull on Stomach .. .. 36
Tweedie on Continued Fevers 36
Walker on Diphtheria .. .. 37
Ward on Liver .. .. .. 37
What to Observe at the Bedside 25
Wright on Headaches .. .. 39

## MICROSCOPE.

Beale on Microscope in Medicine 8
Carpenter on Microscope .. .. 12
Schacht on do. .. .. 32

## MISCELLANEOUS.

Acton on Prostitution .. .. 6
Barclay's Medical Errors .. .. 7
Bascome on Epidemics .. .. 8
Beale on Disease Germs .. .. 8
Buckle's Hospital Statistics .. 11
Chapman's Med. Institutions .. 12
Cooley's Cyclopædia .. .. .. 13
Davies on the Unity of Medicine .. .. .. .. .. .. 14
Gaskoin's De Villalobos .. .. 17
Glenn's Laws affecting Medical Men .. .. .. .. .. .. 18
Gordon on China .. .. .. 18
Graves' Physiology and Medicine 18
Guy's Hospital Reports .. .. 18
Harrison on Lead in Water .. 19
Howe on Epidemics .. .. .. 21
London Hospital Reports. .. 24
Mayne's Medical Vocabulary .. 26
Oppert on Hospitals .. .. .. 27
Part's Case Book .. .. .. 28
St. George's Hospital Reports .. 31
St. Thomas's do. do. .. 31
Snow on Chloroform .. .. .. 33
Veitch on Sick Nursing .. .. 37
Waring's Tropical Resident at Home .. .. .. .. .. 37

## MISCELLANEOUS—*continued.*

PAGE
Whitehead on Transmission .. 38
Wise's Med. amongst Asiatics .. 38
Wolff on Zymotic Diseases .. 39

## OBSTETRICS.

Barnes on Obstetric Operations 8
Hodges on Puerperal Convulsions 20
Lee's Consultations in Midwifery 24
Leishman's Mechanism of Parturition .. .. .. .. .. 24
Pretty's Aids during Labour .. 29
Priestley on Gravid Uterus .. 30
Ramsbotham's Obstetrics .. .. 30
Sinclair & Johnston's Midwifery 33
Smellie's Obstetric Plates .. .. 33
Smith's Manual of Obstetrics .. 33
Swayne's Aphorisms .. .. .. 34
Tanner's Practical Midwifery .. 35
Waller's Midwifery .. .. .. 37

## OPHTHALMOLOGY.

Cooper on Injuries of Eye .. 31
Do. on Near Sight .. .. 13
Dalrymple on Eye .. .. .. 14
Dixon on the Eye .. .. .. 15
Jago on Entoptics .. .. .. 22
Jones' Ophthalmic Medicine .. 23
Do. Defects of Sight .. .. 23
Do. Eye and Ear .. .. .. 23
Liebreich's Atlas of Ophthalmoscopy .. .. .. .. .. 24
Macnamara on the Eye .. .. 25
Power's Illustrations of Diseases of the Eye .. .. .. 29
Walton on the Eye .. .. .. 37
Wells Treatise on the Eye .. 38
Do. on Spectacles .. .. .. 38

## PHYSIOLOGY.

Beale on Protoplasm .. .. .. 8
Do. Life Theories .. .. 8
Carpenter's Human .. .. .. 12
Do. Manual .. .. .. 12
Heale on Vital Causes .. .. 19
Richardson on Coagulation .. 30
Shea's Animal Physiology .... 32

## PSYCHOLOGY, including Diseases of Brain and Nervous System.

Althaus on Epilepsy, Hysteria, &c. 7
Bateman on Aphasia .. .. 8
Browne's Medical Jurisprudence of Insanity .. .. .. .. 11
Bucknill and Tuke's Psychological Medicine .. .. .. 12
Davey on Nature of Insanity .. 14
Downing on Neuralgia .. .. 15
Elam on Brain Diseases .. .. 15
Jones (Handfield) on Functional Nervous Disorders .. .. .. 22
Morris on Irritability .. .. .. 26
Murray on Emotional Diseases 27

## PSYCHOLOGY—*continued.*

PAGE
Reade on Syphilitic Affections of the Nervous System .. .. 30
Reynolds on the Brain .. .. 30
Do. on Epilepsy .. .. 30
Rowe on Nervous Diseases .. 31
Sabben and Browne's Law and Lunacy .. .. .. .. .. 31
Sankey on Mental Diseases .. 31
Sieveking on Epilepsy .. .. 33
Van der Kolk on Mental Disease 37
West Riding Asylum Reports .. 38
Winslow's Obscure Dis. of Brain 39

## PULMONARY and CHEST DISEASES, &c.

Alison on Pulmonary Consumption .. .. .. .. .. .. 6
Bennet on Consumption .. .. 9
Bright on the Chest .. .. .. 10
Cotton on Stethoscope .. .. 14
Davies on Lungs and Heart .. 14
Dobell on the Chest .. .. .. 15
Do. on Tuberculosis .. .. 15
Do. on Winter Cough .. .. 15
Do. First Stage of Consumption .. .. .. .. .. 15
Fuller on the Lungs .. .. .. 16
Do. on Heart .. .. .. .. 16
Garrett on the Windpipe and Consumption .. .. .. .. 17
Jones (Jas.) on Consumption .. 23
Laennec on Auscultation .. .. 23
Markham on Heart .. .. .. 26
Myers on Diseases of Heart among Soldiers .. .. .. 27
Peacock on the Heart .. .. 28
Pirrie on Hay Asthma .. .. 29
Salter on Asthma .. .. .. 31
Skoda on Auscultation .. .. 26
Thompson on Consumption .. 35
Thorowgood on Asthma .. .. 35
Turnbull on Consumption .. 36
Waters on the Chest .. .. .. 38
Do. on Emphysema .. .. 38

## RENAL and URINARY DISEASES.

Basham on Renal Diseases .. 8
Beale on Kidney Diseases .. 8
Do. on Urinary Deposits .. 8
Bird's Urinary Deposits .. .. 10
Harley on Urine .. .. .. .. 19
Parkes on Urine .. .. .. .. 28
Todd on Urinary Organs .. .. 36

## SCIENCE.

Bentley's Manual of Botany .. 9
Brooke's Natural Philosophy .. 11
Hardwich's Photography .. .. 19
Hinds' Harmonies .. .. .. 20
Howard on the Clouds .. .. 21
Huxley on Classification of Animals .. .. .. .. .. 22
Do. Anatomy of Vertebrates .. 22
Jones (Bence) on Matter and Force .. .. .. .. .. 22
Jones (Wharton) on Vision .. 23
Do. on Body, Sense, and Mind 23
Mayne's Lexicon of Terms .. 26
Noad on the Inductorium .. 27
Ord's Comparative Anatomy .. 28

## SCIENCE—*continued.*


PAGE

Pratt's Genealogy of Creation .. 29
Do. Eccentric & Centric Force 29
Do. on Orbital Motion .. .. 29
Do. Astronomical Investigations 29
Do. Oracles of God .. .. .. 29
Price's Photography .. .. .. 30
Reymond's Animal Electricity 30
Taylor's Medical Jurisprudence 35
Vestiges of Creation .. .. .. 36


## SURGERY.


Adams on Reparation of Tendons 6
Allen on Aural Catarrh .. .. 6
Allingham on Rectum .. .. 6
Anderson on the Skin .. .. 7
Arnott on Cancer .. .. .. 7
Ashton on Rectum .. .. .. 7
Brodhurst on Anchylosis .. .. 11
Bryant on Diseases of Joints .. 11
Do. Clinical Surgery .. 11
Callender on Rupture .. .. 12
Chapman on Ulcers .. .. .. 12
Do. Varicose Veins .. .. 12
Clark on Visceral Lesions .. 13
Do. Outlines of Surgery .. .. 13
Collis on Cancer .. .. .. .. 13
Cooper's Surgical Dictionary 14
Coulson on Stone in Bladder .. 14
Curling on Rectum .. .. .. 14
Do. on Testis .. .. .. 14
De Morgan on Cancer .. .. 15
Druitt's Surgeon's Vade-Mecum 15
Fayrer's Clinical Surgery .. 15
Fergusson's Surgery .. .. .. 16
Do. Progress of Surgery 16
Gamgee on Fractures .. .. 17
Gant's Principles of Surgery .. 17


## SURGERY—*continued.*


PAGE

Gant's Practice of do. .. .. 17
Gay on Varicose Disease .. .. 17
Heath's Minor Surgery and Bandaging .. .. .. .. 20
Do. on the Jaws .. .. .. .. 20
Higginbottom on Nitrate of Silver 20
Hill on Stricture .. .. .. 20
Hodgson on Prostate .. .. .. 20
Holt on Stricture .. .. .. 21
Holthouse on Tumours of the Groin .. .. .. .. .. 21
Jordan on Inflammations .. 23
Lawrence's Surgery .. .. .. 23
Do. Ruptures .. .. .. 23
Lee's Practical Pathology .. 24
Liston's Surgery .. .. .. .. 24
Logan on Skin Diseases .. .. 24
Maccormac's Ambulance Surgeon 25
Macleod's Surgery of the Crimea 25
Maclise on Fractures .. .. .. 25
Marsden on Cancer .. .. .. 26
Maunder's Operative Surgery .. 26
Nayler on Skin Diseases .. .. 27
Pirrie's Surgery .. .. .. 29
Price on Excision of Knee-joint 29
Sansom on Chloroform .. . 32
Savage on the Female Pelvic Organs .. .. .. .. .. 32
Smith (Hy.) on Stricture .. .. 33
Do. on Hæmorrhoids .. .. 33
Do. on the Surgery of the Rectum 33
Do. (Dr. J.) Dental Anatomy and Surgery .. .. .. 33
Spender on Ulcers .. .. .. 34
Steggall's Surgical Manual .. 34
Swain on the Knee-Joint .. .. 34
Thompson on Stricture .. .. 35
Do. on Prostate .. .. 35


## SURGERY—*continued.*


PAGE

Thompson on Lithotomy and Lithotrity .. .. .. .. 35
Thompson on Urinary Organs 35
Tomes' Dental Surgery .. .. 37
Wade on Stricture .. .. .. 36
Webb's Surgeon's Ready Rules 38
Wilson on Skin Diseases .. .. 39
Do. Portraits of Skin Diseases 39


## VETERINARY MEDICINE.


Armatage's Emergencies .. 7
Blaine's Veterinary Art .. .. 10
Bourguignon on the Cattle Plague 10
Haycock on Shoeing Horses .. 19
Tuson's Pharmacopœia .. .. 36


## WOMEN AND CHILDREN, Diseases of.


Bennet on Uterus .. .. .. 9
Dillnberger (ed. by Nicol) on Treatment of Women's and Children's Diseases .. .. 27
Ellis on Children .. .... .. 15
Harrison on Children .. .. 19
Hood on Scarlet Fever, &c. .. 21
Kiwisch (ed. by Clay) on Ovaries 13
Lee's Ovarian & Uterine Diseases 24
Do. on Speculum .. .. .. 24
Norton on Infantile Diseases .. 27
Tilt on Uterine Inflammation .. 36
Do. Uterine Therapeutics .. 36
Do. on Change of Life .. .. 36
Underwood on Children .. .. 36
West on Women .. .. . 38
Wright on Uterine Disorders .. 39

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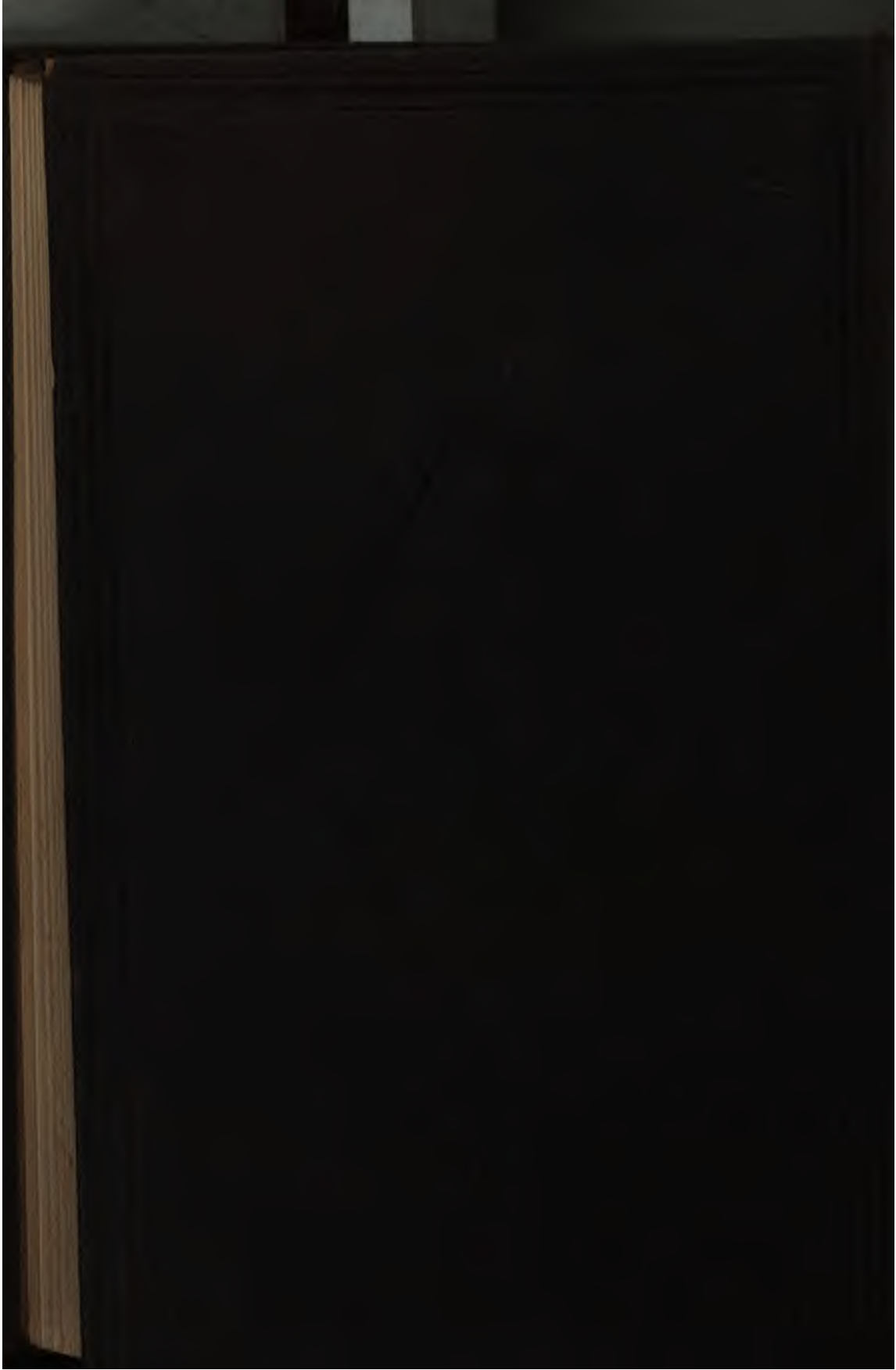
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